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Synthesis and Structural Characterization of an Isomorphous Series of Bis(imidazolin-2-imine) Metal Dichlorides Containing the First Row Transition Metals Mn, Fe, Co, Ni , Cu, and Zn

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Dedicated, in memoriam, to Prof. Dr. Herbert Schumann

Keywords: N Ligands; Chelates; Transition metals; Imidazolin-2-imines

The bis(imidazolin-2-imine) ligand N,N'-bis(1,3-diisopropyl-4,5dimethylimidazolin-2-ylidene)-1,2-ethanediamine (BL^{*i*Pr}) has been used to synthesize a complete series of transition metal dichloride complexes of the type [(BL^{*i*Pr})MCl₂] with M = Mn, Fe, Co, Ni, Cu, Zn. The molecular structure of each complex was established by Xray diffraction analysis; the complexes are isomorphous and

Introduction

The coordination chemistry of poly(guanidine) ligands is currently receiving considerable interest,^[1] since these ligands generally act as efficient electron-donor ligands towards transition metals and are able to form particularly strong metal-nitrogen bonds.^[2,3,4,5] These unique properties are attributable to the ability of the guanidine CN_3 moiety to delocalize a positive charge, affording compounds with enhanced basicity and nucleophilicity. This tendency is even more pronounced in imidazolin-2imines, since the imidazole ring is particularly effective in charge.^[7] stabilizing positive Accordingly, а poly(imidazolin-2-imine) ligands such as the bidentate nitrogen donor ligand N,N'-bis(1,3-diisopropyl-4,5dimethylimidazolin-2-ylidene)-1,2-ethanediamine (BL^{iPr}) can be described by the limiting resonance structures A and **B** (Scheme 1), with the contribution of the ylidic form **B** increasing considerably upon metal coordination. The resulting excellent donor properties of the ligands BL^{R} (R = Me, *i*Pr) were documented by their ability to stabilize coordinatively unsaturated 16-electron halfsandwich complexes and by the preparation of highly reactive copper(I) complexes.^[8,9,10] In addition, it was demonstrated that the strong polarisation of the exocyclic C=N bond in zinc complexes of the type $[(BL^{Me})ZnX_2]$ (X = Cl, OAc) is beneficial for the observation of high crystallize in the monoclinic space group C2/c, allowing a comparison of their structural parameters in a constant packing environment. The complexes exhibit distorted tetrahedral geometries around the metal atoms with the dihedral angles between the MN₂ and MCl₂ planes ranging from 53.9° (M = Cu) to 75.5° (M = Zn).



Scheme 1. Resonance structures **A** and **B** for the bis(imidazolin-2-imine) ligands BL^{R} (R = *i*Pr, Me).

In view of the large number of applications that have been reported for 3d-metal complexes of related 1,4-diaza-1,3-butadiene (α -diimine) ligands,^[12] e. g. the use of iron, cobalt and nickel complexes as polymerization catalysts,^[13] we became interested in studying the reactivity of BL^{*i*Pr} toward first row transition metal dichlorides with the metal ranging from manganese to zinc. We assumed that the diimine ligand BL^{iPr} is able to stabilize four-coordinate metal complexes, since it should provide enough electron density and, together with the anionic chloride ligands, sufficient steric bulk to prevent further coordination of a second BL^{*i*Pr} equivalent or additional solvent molecules. Accordingly, the preparation and structural characterization of a complete series of transition metal complexes of the type $[(BL^{iPr})MCl_2]$ (M = Mn, Fe, Co, Ni, Cu, Zn) is presented

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in this contribution. Because all the complexes crystallized isomorphously, a detailed comparison of their structural parameters can be undertaken without the need to consider different packing effects.

Results and Discussion

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The complexes $[(BL^{iPr})MCl_2]$ (M = Mn, 1; M = Fe, 2; M = Co, 3; M = Ni, 4; M = Cu, 5; M = Zn, 6) were prepared by the reaction of the diimine ligand BL^{iPr} with a suitable metal(II) chloride source (Scheme 2, see experimental part). Addition of an excess of the BL^{iPr} ligand leads neither to the coordination of a second BL^{iPr} equivalent nor to the replacement of chloride anions from the inner coordination sphere, as was observed for CoCl₂ complexes containing related guanidine-hybrid ligands.^[5b] For all complexes, the composition [(BL^{iPr})MCl₂] was confirmed by elemental analysis. Since complexes 1 - 5 are paramagnetic, only the diamagnetic zinc complex 6 was additionally characterized by NMR spectroscopy. Its ¹H NMR spectrum in acetone- d_6 exhibits one septet at 5.00 ppm together with one doublet at 1.35 ppm, indicating that rotation around the exocyclic C-N bonds is fast on the NMR time scale. In addition, two singlets are observed at 3.40 ppm and 2.12 ppm, which can be assigned to the C_2H_4 -bridge and the methyl groups at the C4/5 positions of the imidazoline rings, respectively.



Scheme 2. Synthesis of the metal complexes 1 - 6.

Re-crystallization by diffusion of n-hexane into THF solutions of the complexes afforded colourless (1, 6), beige (2), blue (3) and red (4) single crystals, whereas brown crystals of the copper complex 5 were obtained by diffusion of diethyl ether into an acetonitrile solution. The crystal structures of 1 - 6 were determined by X-ray diffraction analyses (Figure 1); 1 - 6 are isomorphous and crystallize in the monoclinic space group C2/c with Z = 4. All complexes display crystallographic C_2 -symmetry about an axis passing through the metal atom and the centre of the C1-C1a bond, allowing a detailed comparison of the structures without the need to consider differences in packing. Related studies were published by Leigh and Kubiak for complexes of metal(II) halides with the ligands *N*,*N*,*N*',*N*'-tetramethylpropyl-1,3-diamine

(tmpn) and 6,6'-(2,4,6-triisopropylphenyl)-2,2'bipyridine (tripbipy).^[14,15] In both series, however, two different space groups were observed for the complexes [(tmpn)MCl₂] (M = Mn – Cu) and [(tripbipy)MCl₂] (M = Fe – Zn), respectively.

((Figure 1 here))

In the solid state, the $[(BL^{iPr})MCl_2]$ moieties of the complexes 1 - 6 are connected with four neighbouring molecules by intermolecular C7-H7B $\cdots\pi$ contacts between isopropyl methyl groups and the imidazole rings, which is illustrated by the packing of compound 4 shown in Figure 2. All metal atoms are four-coordinate and display distorted tetrahedral geometries with the diimine ligand forming a five-membered chelate ring. The N1-M-N1' bite angles range from $81.28(6)^{\circ}$ (in 2) and $84.39(5)^{\circ}$ (in 6) and are thus significantly smaller than expected for an ideal tetrahedral arrangement (109.5°). Accordingly, expanded Cl-M-Cl' angles between 113.95(3)° (in 3) and $118.84(3)^{\circ}$ (in 1) are observed (Table 1); in the copper complex 5, however, a relatively small Cl-Cu-Cl' angle of $104.35(3)^{\circ}$ is found, which is in agreement with 5 being most strongly distorted toward a square planar geometry (vide infra). Since all complexes display C_2 symmetry in the solid state, the degree of distortion from an ideal tetrahedron toward a square can be described by the dihedral angle between the N1-M-N1' and Cl-M-Cl' planes, respectively, which can adopt values between 90° (tetrahedron) and 0° (square). In all cases (Table 1), these angles deviate significantly from 90° and follow the order **6** $(75.5^{\circ}) > 1$ $(74.5^{\circ}) > 3$ $(72.8^{\circ}) > 2$ $(72.2^{\circ}) > 4$ $(68.6^{\circ}) >$ **5** (53.9°).

((Figure 2 here))

Another method for describing the distortion from ideal geometries in four-coordinate complexes was proposed by *Houser*,^[16] who introduced the geometry index $\tau_4 =$ $[360^{\circ} - (\alpha + \beta)]/141^{\circ}$, where α and β represent the largest angles in the four-coordinate species. The values of τ_4 will range from 1.0 for a perfect tetrahedron to zero for a perfect square planar geometry. Intermediate structures, including trigonal pyramidal and seesaw, will afford values $0 < \tau_4 < 1.0$. In our series 1 - 6, the largest angles are N1-M-Cl and N1'-M-Cl', which are identical because of the crystallographic C_2 -symmetry (Table 1). The calculated τ_4 follow almost the same order as the dihedral angles mentioned above with 6 (0.82) ≈ 1 (0.82) > 2 (0.79) > 3 (0.78) > 4 (0.75) > 5 (0.57). Again, the manganese and zinc complexes 1 and 6 show the smallest deviation from a tetrahedral geometry, whereas the copper complex 5 exhibits the strongest distortion. Similar τ_4 values have been established for the complexes $[(tripbipy)MCl_2]$ (M = Fe – Zn),^[15] and this trend is also in accord with an increasing impact of Jahn-Teller distortion, which should be absent for the d^5 -, d^7 - and d^{10} complexes 1, 3 and 6 and is expected to be most strongly pronounced for the Cu(II) d^9 -system 5.^[17] It should be noted that, in the related copper(II)-hydroxo complex $[Cu^{II}(\mu-OH)(BL^{iPr})]_2[PF_6]_2$, the BL^{iPr} ligand has also proved capable of stabilizing a square planar environment.[10a]

Partial charge separation and delocalization in the coordinated BL^{iPr} ligand (Scheme 1) can be deduced from

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the observation of large M-N1-C2-N2 torsion angles of about 60° in all complexes (Table 1), indicating a perturbed π -interaction between the coordinated nitrogen atoms and the imidazole rings. Consequently, the exocyclic C2-N1 bonds are elongated and approach the intra-ring C2-N2 and C2-N3 distances. The degree of charge separation can be illustrated by the parameter $\rho =$ 2a/(b+c), with a, b and c representing the exo- (a) and endocyclic (b, c) distances within the CN₃ guanidine molety.^[5b,5d] The ρ values in all complexes are very similar ($\rho \approx 0.97$) and indicate substantial charge delocalization, albeit to a smaller extent than found for cyclopentadienyl- and arene-ruthenium complexes.^[8a] Since the imidazole rings in 1 - 6 are not fully perpendicular with the N1-M-N1' plane, the resulting C_{2} symmetric propeller-like conformation of the BL^{*i*Pr} ligand can also be held partly responsible for the observation of distorted tetrahedral geometries (vide supra), which seem to be a compromise between electronic and steric factors.



Figure 3. M-N (\blacktriangle) and M-Cl (\blacksquare) bond lengths [Å] in complexes 1-6.

The M-N1 bond lengths follow the expected trend as predicted by the ionic radii of the respective metal atoms (Table 1),^[f8] except for the copper complex 5, which exhibits the shortest M-N [Cu-N1 = 1.9709(12) Å] and M-Cl bond lengths [Cu-Cl = 2.2460(5) Å]; this behaviour might be attributed to the fact that 5 exhibits a significantly stronger distortion from a tetrahedral geometry than the other complexes. The M-Cl bonds also follow the same trend, even though the differences are much less pronounced (Figure 3). Comparison with the related series [(tripbipy)MCl₂] (M = Fe - Zn) shows a similar trend for the M-N and M-Cl bond lengths; in all cases, however, shorter M-N bonds together with longer M-Cl bonds are observed for complexes 1 - 6, indicating that the BL^{*i*Pr} is a significantly stronger N-donor ligand than the bipyridine ligand tripbipy.^[15] The metal-nitrogen bonds in 1 - 6 are also shorter than those found for guanidine complexes containing a related ethylenebridged bis(imidazolidin-2-imine) ligand,^[5b,5c] revealing that the presence of an unsaturated heterocycle in BL^{i} affords a ligand with slightly enhanced donor properties, presumably because of a stronger contribution from the resonance structure **B** (Scheme 1).^[7c] In contrast, the Zn-N bonds in 6 [2.0342(9) Å] are slightly longer than those found for the complex [$(BL^{Me})ZnCl_2$], for which two different Zn-N distances of 2.019(1) and 2.032(1) Å were determined.[11] Even shorter metal-nitrogen bond distances were observed for a series of tetrahedral complexes $[(hppH)_2MCl_2]$ (M = Mn, Fe, Co, Ni) with hppH = 1,3,4,6,7,8-hexahydro-2H-pyrimido[1,2-a]pyrimidine, in which the guanidine ligands bond to the metal atoms with additional interaction between the secondary NH groups and the metal-bound chlorides.^[19]

Conclusions

The ligand BL^{*i*Pr} proved to be a suitable ligand for controlling the coordination number and geometry of six first row transition metals. Its reaction with metal(II) chlorides (M = Mn, Fe, Co, Ni, Cu, Zn) afforded in all cases mononuclear complexes with distorted tetrahedral coordination environments, which seems to be the strongly favoured coordination mode for the BL^{*i*Pr} ligand in comparison with the alternative square planar or octahedral geometries. Particularly with regard to the large number of applications that have been reported for 3d-metal complexes of related α -diimine ligands,^[12] the potential use of complexes 1 - 6 as homogeneous catalysts, e. g. for olefin polymerisation, can be envisaged.

Experimental Section

General: All operations were performed in an atmosphere of dry argon by using Schlenk and vacuum techniques. All solvents were purified by standard methods and distilled prior to use. ¹H and ¹³C NMR spectra were recorded on a Bruker DPX 400 device. The chemical shifts are given in ppm relative to TMS. The spin coupling patterns are indicated as s (singlet), d (doublet) and sept (septet). Elemental analyses (C, H, N) were performed on a Elementar Vario EL III CHNS elemental analyzer. Mass spectrometry was performed with a Finnigan MAT 90 device. CoCl₂(anhydr.), NiCl₂(DME) were obtained from Aldrich and CuCl₂ from Riedel-deHaën. FeCl₂(THF)_{1.3} and the BL^{*i*Pr} ligand were synthesized according to published procedures.^[20, 8b]

Synthesis of $[(\mathbf{BL}^{i\mathbf{Pr}})\mathbf{MnCl}_2]$ (1): A solution of $\mathbf{BL}^{i\mathbf{Pr}}$ (200.0 mg, 0.48 mmol) in THF (10 mL) was added to a suspension of MnCl₂ (59.8 mg, 0.475 mmol) in THF (20 mL). The mixture was stirred for 48 h. The volume was reduced to 5 mL and the product was precipitated with *n*-hexane (30 mL). Filtration, washing with *n*-hexane (2 × 10 mL) and drying *in vacuo* afforded the product as a light yellow solid (yield: 213.7 mg, 82.1%). Found: C, 53.28; H, 8.11; N, 15.28. Calc. for C₂₄H₄₄N₆MnCl₂: C, 53.14; H, 8.18; N, 15.49%.

Synthesis of [(BL^{*i*Pr})**FeCl₂] (2):** A solution of BL^{*i*Pr} (217 mg, 0.521 mmol) in THF (10 mL) was added to a solution of FeCl₂(THF)_{1.3} (66 mg, 0.521 mmol) in THF (20 mL). The mixture was stirred overnight. A white precipitate formed and the product was fully precipitated with *n*-hexane (30 mL). Filtration, washing with *n*-hexane (2 × 10 mL) and drying *in vacuo* afforded the product as a beige solid (yield: 221 mg, 78%). Found: C, 53.29; H, 8.25; N, 15.32. Calc. for C₂₄H₄₄N₆FeCl₂: C, 53.05; H, 8.16; N, 15.47%.

Synthesis of [(**B**L^{*i*Pr})**CoCl**₂] (**3**): A solution of BL^{*i*Pr} (166.7 mg, 0.40 mmol) in THF (5 mL) was added to a suspension of CoCl₂ (50.0 mg, 0.39 mmol) in THF (15 mL). The mixture was stirred overnight. The volume was reduced to 5 mL and the product was precipitated with *n*-hexane (30 mL). Filtration, washing with *n*-hexane (2 × 5 mL) and drying *in vacuo* afforded the product as a blue solid (yield: 97.4 mg, 45.6%). Found: C, 53.23; H, 8.38; N, 14.96. Calc. for C₂₄H₄₄N₆CoCl₂: C, 52.75; H, 8.12; N, 15.38%. MS (EI, 70 eV): m/z = 545 (M⁺), 208 (BL^{*i*Pr}/2).

Synthesis of [(**BL**^{*i*Pr})**NiCl**₂] (4): A solution of **BL**^{*i*Pr} (263 mg, 0.63 mmol) in THF (10 mL) was added dropwise to a solution of [Ni(DME)Cl₂] (132 mg, 0.60 mmol) in THF (10 mL) at room temperature. During addition of the ligand the color changes to deep-red; the solution was stirred for 12 hours followed by reduction of THF volume to 10 mL. The product was fully precipitated upon addition of *n*-hexane (40 mL). Filtration, washing with *n*-hexane (2 × 10 mL) and drying in vacuo afforded the product as a deep-red solid (324 mg, 99%). Found: C, 53.16; H, 8.28; N, 14.89. Calc. for C₂₄H₄₄N₆NiCl₂: C, 52.77; H, 8.12; N, 15.38%. MS (EI, 70 eV) *m*/*z* = 546 (M⁺), 511 (M⁺ – Cl, 20), 416 (BL^{*i*Pr+}).

Synthesis of [(**BL**^{*i*Pr})**CuCl**₂] (5): A solution of **BL**^{*i*Pr} (125.4 mg, 0.30 mmol) in acetonitrile (5 mL) was added to a suspension of CuCl₂ (40.0 mg, 0.30 mmol) in acetonitrile (15 mL). The mixture was stirred overnight. The acetonitrile was removed *in vacuo* and the residue redissolved in THF (5 mL). The product was precipitated with *n*-hexane (30 mL). Filtration, washing with *n*-hexane (2 × 5 mL) and drying *in vacuo* afforded the product as a blue solid (yield: 110.8 mg, 66.7%). Found: C, 53.23; H, 8.38; N, 15.32. Calc. for C₂₄H₄₄N₆CuCl₂: C, 52.31; H, 8.05; N, 15.25%.

Synthesis of $[(BL^{iPr})ZnCl_2]$ (6): A solution of BL^{iPr} (150.0 mg, 0.36 mmol) in THF (10 mL) was added to a solution of $ZnCl_2$ (49.1 mg, 0.36 mmol) in THF (15 mL). The mixture was stirred overnight, during which the product precipitated. The volume was reduced to 5 mL and the product was completely precipitated with *n*-hexane (30 mL). Filtration, washing with *n*-hexane (2 × 5 mL) and drying *in vacuo* afforded the product as a white solid (yield: 180.3 mg, 91.7%). Found: C, 52.28; H, 8.06; N, 14.503. Calc. for C₂₄H₄₄N₆ZnCl₂: C, 52.13; H, 8.02; N, 15.20%. MS (EI, 70 eV): *m*/*z* = 552 (M⁺), 208 (BL^{iPr}/2). ¹H-NMR (400 MHz, acetone-*d*₆, 25°C): δ [ppm] = 5.00 (sept, 4H, C*H*(CH₃)₂, ³J = 7.1 Hz), 3.40 (s, 4H, CH₂), 2.12 (s, 12H, CCH₃), 1.35 (d, 24H, CH(CH₃)₂, ³J = 7.1 Hz); ¹³C-NMR (100 MHz, acetone-*d*₆, 25°C): δ [ppm] = 155.9 (C2), 119.8 (CCH₃), 54.5 (CH₂), 48.4 (NCH(CH₃)₂), 22.1 (CCH₃), 10.5 (NCH(CH₃)₂).

X-ray Crystal Structure Determinations. Data were recorded on area detectors (Nonius Diffraction for **2**, otherwise Oxford Diffraction) at low temperature. Absorption corrections were performed on the basis of multi-scans. Structures were refined anisotropically using the program SHELXL-97.^[21] Hydrogen atoms were included using rigid methyl groups or a riding model. Numerical details are summarized in Table 2. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-745604–9 for **1–6** respectively. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax.: (internat.) + 44 1223/336-033; e-mail: deposit@ccdc.cam.ac.uk].

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- a) S. Herres-Pawlis, A. Neuba, O. Seewald, T. Seshadri, H. Egold, U. Flörke, G. Henkel, *Eur. J. Org. Chem.* 2005, 4879-4890; b) S. Herres-Pawlis, *Nachr. Chem.* 2009, *57*, 20-23.
- [2] a) C. Würtele, E. Gaoutchenova, K. Harms, M. C. Holthausen, J. Sundermeyer, S. Schindler, *Angew. Chem.* 2006, 118, 3951-3954; *Angew. Chem. Int. Ed.* 2006, 45, 3867-3869; b) D. Maiti, D.-H. Lee, A. A. Narducci

Sarjeant, M. Y. M. Pau, E. I. Solomon, K. Gaoutchenova, J. Sundermeyer, K. D. Karlin, *J. Am. Chem. Soc.* **2008**, *130*, 6700-6701.

- [3] a) P. Roquette, A. Maronna, A. Peters, E. Kaifer, H.-J. Himmel, C. Hauf, V. Herz, E.-W. Scheidt, W. Scherer, *Chem. Eur. J.* 2010, *16*, 1336-1350; b) D. Emeljanenko, A. Peters, N. Wagner, J. Beck, E. Kaifer and H.-J. Himmel, *Eur. J. Inorg. Chem.* 2010, 1839-1846; c) M. Reinmuth, U. Wild, D. Rudolf, E. Kaifer, M. Enders, H. Wadepohl and H.-J. Himmel, *Eur. J. Inorg. Chem.* 2009, 4795-4808.
- [4] H. Bruns, M. Patil, J. Carreras, A. Vázquez, W. Thiel, R. Goddard and M. Alcarazo, Angew. Chem. 2010, 122, 3762-3766.
- [5] a) A. Hoffmann, J. Börner, U. Flörke, S. Herres-Pawlis, *Inorg. Chim. Acta* 2009, *362*, 1185-1193; b) A. Neuba, R. Haase, M. Bernard, U. Flörke, S. Herres-Pawlis, *Z. Anorg. Allg. Chem.* 2008, *634*, 2511-2517; c) J. Börner, S. Herres-Pawlis, U. Flörke, K. Huber, *Eur. J. Inorg. Chem.* 2007, 5645-5651; d) J. Börner, U. Flörke, K. Huber, A. Döring, D. Kuckling, S. Herres-Pawlis, *Chem. Eur. J.* 2009, *15*, 2362-2376.
- [6] a) T. Ishikawa, Superbases for Organic Synthesis, John Wiley & Sons, Chichester, 2009; b) T. Ishikawa and T. Kumamoto, Synthesis 2006, 5, 737-752.
- [7] a) G. Frison, A. Sevin, J. Chem. Soc. Perkin Trans. 2 2002, 1692-1697; b) N. Kuhn, M. Grathwohl, M. Steimann, G. Henkel, Z. Naturforsch. Teil B 1998, 53, 997-1003.; c) M. Tamm, D. Petrovic, S. Randoll, S. Beer, T. Bannenberg, P. G. Jones, J. Grunenberg, Org. Biomol. Chem. 2007, 5, 523-530.
- [8] a) T. Glöge, D. Petrovic, C. G. Hrib, P. G. Jones and M. Tamm, *Eur. J. Inorg. Chem.* **2009**, 4538-4546; b) D. Petrovic, T. Glöge, T. Bannenberg, C. G. Hrib, S. Randoll, P. G. Jones, M. Tamm, *Eur. J. Inorg. Chem.* **2007**, 3472-3475; c) T. Glöge, D. Petrovic, C. G. Hrib, P. G. Jones, M. Tamm, *Z. Naturforsch. Teil B* **2008**, *63*, 1155-1159.
- [9] D. Petrovic, C. G. Hrib, S. Randoll, P. G. Jones and M. Tamm, Organometallics 2008, 27, 778-783.
- [10] a) D. Petrovic, L. M. R. Hill, P. G. Jones, W. B. Tolman and M. Tamm, *Dalton Trans.* 2008, 887-894; b) D. Petrovic, T. Bannenberg, S. Randoll, P. G. Jones and M. Tamm, *Dalton Trans.* 2007, 2812-2822.
- [11] J. Börner, U. Flörke, T. Glöge, T. Bannenberg, M. Tamm, M. D. Jones, A. Döring, D. Kuckling, S. Herres-Pawlis, J. Mol. Catal. A. Chem. 2010, 316, 139-145.
- [12] a) G. van Koten and K. Vrieze, Adv. Organomet. Chem. 1982, 21, 151-239; b) E. König, Coord. Chem. Rev. 1968, 3, 471-495.
- [13] a) S. D. Ittel, L. K. Johnson, M. Brookhart, *Chem. Rev.* 2000, 100, 1169-1203; b) G. J. P. Britovsek, V. C. Gibson, D. F. Wass, *Angew. Chem.* 1999, 111, 448-468; *Angew. Chem. Int. Ed.* 1999, 38, 428-447.
- [14] D. A. Handley, P. B. Hitchcock, T. H. Lee, G. J. Leigh, *Inorg. Chim. Acta* 2001, 314, 14-21.
- [15] E. E. Benson, A. L. Rheingold, C. P. Kubiak, *Inorg. Chem.* 2010, 49, 1458-1464.
- [16] L. Yang, D. R. Powell, R. P. Houser, *Dalton Trans.* **2007**, 955-964; this four-coordinate geometry index τ_4 is related to the five-coordinate geometry index $\tau_5 = (\alpha \beta)/60^\circ$, which has been developed for describing distortions between trigonal-bipyramidal ($\tau_5 = 1$) and square-pyramidal geometries ($\tau_5 = 0$), see: A. W. Addison, T. N. Rao, J. Reedijk, J. van der Rijn, G. C. Verschoor, *J. Chem. Soc. Dalton Trans.* **1984**, 1349-1356.
- [17] a) D. Reinen, M. Atanasov, G. Nikolov, F. Steffens, *Inorg. Chem.* **1988**, 27, 1678-1686; b) D. Reinen, *Comments Inorg. Chem.* **1983**, 2, 227-246.
- [18] R. D. Shannon, Acta Cryst. 1976, A32, 751-767.

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- [19] S. H. Oakley, D. B. Soria, M. P. Coles, P. B. Hitchcock, *Polyhedron* 2006, 25, 1247-1255.
- [20] H. Zhao, R. CleHrac, J.-S. Sun, X. Ouyang, J. M. Clemente-Juan, C. J. Gómez-García, E. Coronado, K. R. Dunbar, J. Solid State Chemistry 2001, 159, 281-292.
- [21] G. M. Sheldrick, Acta Cryst. 2008, B64, 112-122.

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Figure 1. ORTEP diagram of the complexes $[(BL^{iPr})MCl_2]$ (M = Mn, 1; M = Fe, 2; M = Co, 3; M = Ni, 4; M = Cu, 5; M = Zn, 6) with thermal displacement parameters drawn at 50% probability; selected bond lengths and angles are shown in Table 1.



Figure 2. Packing of compound **4** showing the H7B $\cdots\pi$ contacts (2.69 Å) as thick dashed bonds; The H7B-. The view direction is perpendicular to the ab plane in the region z ca. 1/4.

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	1 (M = Mn)	2 (M = Fe)	3 (M = Co)	4 (M = Ni)	5 (M = Cu)	6 (M = Zn)
M-N1	2.1224(12)	2.0668(16)	2.0142(14)	1.9951(9)	1.9709(12)	2.0342(9)
M-Cl	2.3356(5)	2.2795(7)	2.2585(5)	2.2502(4)	2.2460(5)	2.2500(4)
N1-C2	1.3248(17)	1.330(2)	1.329(2)	1.3308(14)	1.3286(18)	1.3264(14)
N2-C2 ^[a]	1.3651(18)	1.364(2)	1.362(2)	1.3680(14)	1.3592(17)	1.3664(14)
N3-C2 ^[a]	1.3645(18)	1.367(2)	1.362(2)	1.3614(14)	1.3644(18)	1.3615(13)
N1-M-N1'	81.46(6)	81.28(6)	84.00(8)	83.58(5)	83.39(7)	84.39(5)
Cl-M-Cl'	118.64(3)	118.05(3)	113.95(3)	114.64(3)	104.35(3)	115.46(2)
N1-M-Cl	122.45(3)	124.14(5)	124.83(4)	127.38(3)	140.14(4)	122.54(3)
N1-M-Cl'	103.70(3)	102.70(5)	103.83(4)	101.43(3)	98.52(4)	104.67(3)
M-N-C-N	59.84	58.76	60.12	59.16	57.59	61.25
Angle between MCl_2 and MN_2 planes	74.5	72.2	72.8	68.6	53.9	75.5
Angle sum around N1	357.0	357.7	357.3	357.7	358.6	356.7
ρ	0.971	0.974	0.976	0.975	0.976	0.972
$ au_4^{[a]}$	0.82	0.79	0.78	0.75	0.57	0.82
Angle between imidazole planes	67.1	66.0	66.1	66.6	64.8	66.2
Ionic radii in Å ^[b]	0.66	0.63	0.58	0.55	0.57	0.60

[a] $\tau_4 = [360^\circ - (\alpha + \beta)]/141^\circ$, where α and β represent the largest angles in four-coordinate species; here $\alpha = \beta$, because of the crystallographic C_2 symmetry of complexes **1** - **6**. [b] Effective ionic radii for tetrahedral complexes, see ref. [18].

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Empirical formula	$C_{24}H_{44}Cl_2MnN_6$	$C_{24}H_{44}Cl_2FeN_6$	$C_{24}H_{44}Cl_2CoN_6$	$C_{24}H_{44}Cl_2NiN_6$	$C_{24}H_{44}Cl_2CuN_6$	$C_{24}H_{44}Cl_2ZnN_6$
a (Å)	14.4058(4)	14.4589(2)	14.3819(6)	14.3552(2)	14.2387(4)	14.4222(11)
<i>b</i> (Å)	11.2178(4)	11.2089(10)	11.1473(4)	11.1407(2)	11.0831(2)	11.1543(8)
<i>c</i> (Å)	17.4655(6)	17.5226(2)	17.4156(6)	17.4547(4)	17.5153(4)	17.4094(15)
α (°)	90	90	90	90	90	90
β (°)	99.302(4)	99.6184(6)	99.463(6)	99.402(2)	98.623(2)	99.567(8)
γ (°)	90	90	90	90	90	90
$V(Å^3)$	2785.33(16)	2799.94(6)	2754.06(18)	2753.98(9)	2732.83(11)	2761.7(4)
Ζ	4	4	4	4	4	4
formula weight	542.49	543.40	546.48	546.26	551.09	552.92
space group	C2/c	C2/c	C2/c	C2/c	C2/c	C2/c
<i>T</i> (°C)	-173	-100	-173	-173	-173	-173
λ (Å)	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073
D _{caled} (g cm ⁻³)	1.294	1.289	1.318	1.317	1.339	1.330
$\mu (\mathrm{mm}^{-1})$	0.69	0.75	0.84	0.92	1.02	1.11
R(F _o)	0.0306	0.0363	0.0341	0.0266	0.0290	0.0223
$R_w(F_o^2)$	0.0563	0.0948	0.0673	0.0744	0.0777	0.0607

Thomas Glöge, Dejan Petrovic, Cristian G. Hrib, Constantin Daniliuc, Eberhardt Herdtweck, Peter G. Jones, Matthias Tamm* Page No. – Page No.

Synthesis and Structural Characterization of an Isomorphous Series of Bis(imidazolin-2-imine) Metal Dichlorides Containing the First Row Transition Metals Mn, Fe, Co, Ni , Cu, and Zn



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