

Pseudo-tetrahedral Coordination Compounds of Cobalt, Zinc, Nickel and Iron Halides with 3(5)-Methyl-5(3)-phenylpyrazole. The Crystal and Molecular Structures of Dichlorobis(3-methyl-5-phenylpyrazole)cobalt(II) and Dibromobis(3-methyl-5-phenylpyrazole)zinc(II)

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Abstract

The syntheses, spectroscopic and magnetic properties of the compounds ML_2X_2 (where M = Co, Zn, Ni, Fe; L = 3-methyl-5-phenylpyrazole; X = Cl, Br) are described. Two different crystal modifications have been isolated of both the chlorides and the bromides: α and β for the chlorides and α' and β' for the bromides. The ligand field spectra of the two Co chlorides are identical, suggesting only a difference in crystal packing for the α and β isomers. For both CoL_2Cl_2 and ZnL_2Br_2 , one of the modifications has been investigated structurally by single-crystal X-ray crystallography. Crystal data for $\beta-CoL_2Cl_2$: monoclinic, $P2_1/n$, $a = 8.792(2)$, $b = 20.926(3)$, $c = 11.497(1)$ Å, $\beta = 104.03(1)^\circ$, $V = 2052$ Å³, $Z = 4$, $R = 0.028$, $R_w = 0.033$. Crystal data for $\beta'-ZnL_2Br_2$: monoclinic, $P2_1/n$, $a = 9.039(1)$, $b = 21.325(3)$, $c = 11.521(2)$ Å, $\beta = 105.40(1)^\circ$, $V = 2141$ Å³, $Z = 4$, $R = 0.038$, $R_w = 0.050$. In both $\beta-CoL_2Cl_2$ and $\beta'-ZnL_2Br_2$ the metal coordination is pseudo-tetrahedral, involving two nitrogen donors of L (Co–N 2.031(3) and 2.008(3) Å; Zn–N 2.053(5) and 2.013(5) Å) and two halide atoms (Co–Cl 2.252(1) and 2.222(1) Å; Zn–Br 2.373(1) and 2.345(1) Å). The ligand field spectroscopic data agree with tetrahedral coordination in all the compounds described in this paper.

Introduction

In the past decade the use of ligand-induced decomposition of transition metal tetrafluoroborates has allowed a large number of structural and magnetic studies of fluoride-bridged coordination compounds [1–3]. This procedure has been particularly useful in the case of triazole and pyrazole type ligands. However, single-crystal studies were possible in only a few cases. Some time ago the ligand 3(5)-methyl-5(3)-phenylpyrazole (henceforth de-

noted as L) was reported to introduce decomposition of metal(II) tetrafluoroborates [4]. One of the products, $Cu_2F_2L_4(BF_4)_2$, consists of co-square planar difluoro-bridged Cu(II) dimers with bridging bidentate BF_4^- anions in axial semi-coordination. A strong magnetic exchange coupling exists between the copper ions, with an exchange constant J of -118.5 cm⁻¹. These studies have resulted in the need of related compounds for which both a study of the structure and the properties are possible. Therefore, it was decided to study a number of first-row transition metal chlorides and bromides containing this ligand. The first results of this research, dealing with the compounds of general formula ML_2X_2 (where M = Co, Zn, Ni, Fe and X = Cl, Br), are presented here, including crystal structures of the $CoCl_2$ and the $ZnBr_2$ adducts. Two crystal modifications were found for several compounds.

Experimental

Starting Materials

The synthesis of 3(5)-methyl-5(3)-phenylpyrazole was described earlier [5]. The transition metal salts were used as commercially available.

Synthesis of the Coordination Compounds

Four mmol of $MX_2 \cdot nH_2O$ (M = Co, Zn, Ni, Fe; X = Cl, Br) and 7.6 mmol of L were dissolved in 40 ml of warm ethanol. In the case of M = Ni and X = Br triethylorthoformate was added in order to remove water from the solution. FeL_2Br_2 was prepared in a nitrogen atmosphere using Schlenk techniques. The products ML_2X_2 crystallized upon standing at room temperature. After isolation, the crystals were washed with ethanol and ether and dried in the air. FeL_2Br_2 was dried *in vacuo* at room temperature and stored under nitrogen. Yields were higher than 50% for all compounds. With both M = Co and Zn two modifications, labelled α and β for X = Cl and α' and β' for X = Br, were

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consecutively obtained from the same solution; so far, however, attempts to control the formation of either the $\alpha(\alpha')$ or the $\beta(\beta')$ form by nucleation with crystals of the desired modification have failed. Also recrystallization attempts to convert one isomer to another did not yield unambiguous results.

Both chloride and bromide compounds were obtained with $M = \text{Ni, Fe}$, however, only the bromides were X-ray isomorphous with one of the isomers of the corresponding Zn compounds. For the Ni and Fe chlorides spectroscopic parameters suggested octahedral symmetry around the metal ions. These compounds and their properties will be dealt with in a subsequent paper.

Physical and Analytical Measurements

IR spectra ($4000\text{--}180\text{ cm}^{-1}$) were recorded on a Perkin-Elmer 580 spectrometer equipped with a data station. Samples were prepared as KBr pellets and as nujol mulls.

Ligand field spectra (diffuse reflectance) were recorded on a Perkin-Elmer 330 spectrophotometer, also equipped with a data station (PE type 3600). MgO was used as reference.

^1H NMR spectra were recorded on a Jeol PS-100 (100 MHz) or a Jeol FX-200 (200 MHz) spectrometer. TMS (tetramethylsilane) was used as an internal reference.

Metal analyses were carried out using standard EDTA titration techniques. Cl and Br contents were determined by potentiometric titrations with AgNO_3 . Other elements (C, H, N) were analysed at Pascher's Microanalytical Laboratory (Bonn, F.R.G.).

Static magnetic susceptibility measurements in the 4–80 K region were carried out using a parallel field vibrating sample magnetometer (PAR model 150 A) with a Janis cryostat. The data were corrected for the diamagnetism of the constituents and for the temperature-independent paramagnetism of the metal ions [6].

Data Collection and Refinement

Crystallographic data and relevant information on the data collection and refinement have been summarized in Table 1. For both structures, systematic absences in the diffractometer data were indicative of the monoclinic space group $P2_1/n$. The

TABLE 1. Crystal and diffraction data of $\beta\text{-CoL}_2\text{Cl}_2$ and $\beta'\text{-ZnL}_2\text{Br}_2$

Compound	$\beta\text{-CoL}_2\text{Cl}_2$	$\beta'\text{-ZnL}_2\text{Br}_2$
Molecular formula	$\text{C}_{20}\text{H}_{20}\text{Cl}_2\text{CoN}_4$	$\text{C}_{20}\text{H}_{20}\text{Br}_2\text{N}_4\text{Zn}$
Crystal colour	blue	white
Crystal shape	rod	polyhedron
Crystal dimensions (mm)	$0.2 \times 0.2 \times 0.45$	$0.3 \times 0.3 \times 0.4$
M_w (g mol^{-1})	446.2	541.6
Space group	$P2_1/n$	$P2_1/n$
a (Å)	8.792(2)	9.039(1)
b (Å)	20.926(3)	21.325(3)
c (Å)	11.497(1)	11.521(2)
β (°)	104.03(1)	105.40(1)
V (Å ³)	2052	2141
Z	4	4
D_{meas}^a (M g m^{-3})	1.44(1)	1.67(1)
D_{calc} (M g m^{-3})	1.44	1.68
$F(000)$	916	1072
θ range (°)	2–27	2–24
Octants collected	$h > 0, k > 0$	$h > 0, k < 0$
Scan mode	$\omega\text{--}\theta$	$\omega\text{--}\theta$
Measured reflections	4903	3706
Independent reflections	4607	3503
Significant reflections ($I > 2\sigma(I)$)	1746	1987
Agreement factor between equivalent reflections	0.035	0.064
Data collection	room temperature	room temperature
Radiation used ^b	Mo K α	Mo K α
Diffractometer type	CAD-4	CAD-4
μ (cm^{-1})	11.1	48.8
Final R value	0.028	0.038
Final R_w value	0.033	0.050
Transmission range (azimuth scan)	0.96–1.03	0.86–1.13

^aMeasured by flotation. ^bGraphite-monochromized.

scanning rate was adjusted to the required precision of $\sigma(F) < 0.01 I$, with a maximum scan time of 60 s per reflection. Intensities I and their estimated standard deviations were calculated from counting statistics. The data were corrected for decreases in scattering power of the crystals during the data collection; Lorentz and polarization corrections were applied in the usual way. As the single crystal of β' -ZnL₂Br₂ had an undefined, nearly spherical shape, corrections for absorption and extinction were not applied. Scattering factors, including anomalous dispersion, were taken from ref. 7.

For β -CoL₂Cl₂, the cobalt positions were located in a Patterson synthesis. Using AUTOFOUR, a program for automatic crystal structure determination developed in our laboratory [8], all non-hydrogen atomic positions were obtained. Nearly all hydrogen atoms were located by subsequent least-squares refinement cycles followed by difference Fourier synthesis; two hydrogen positions had to be calculated. The refinement was carried out using weights $1/\sigma^2(F)$, with $\sigma(F) = \sigma(F)$ counting statistics + 0.03 F . The final difference Fourier

synthesis did not show significant features. The final values of the residuals were $R = 0.028$, $R_w = 0.033$ for 1746 significant reflections. Atomic positions and equivalent isotropic thermal parameters of the non-hydrogen atoms are listed in Table 2. See also 'Supplementary Material'.

For β' -ZnL₂Br₂, the Patterson map could be interpreted with the aid of the Patterson solution of the Co compound mentioned above. Input of the Zn positions in AUTOFOUR yielded the positions of the non-hydrogen atoms; the hydrogen positions were calculated. The refinement was carried out as above, with the exception that the thermal parameters of the hydrogen atoms were fixed at $B_{iso} = 7.5 \text{ \AA}^2$. The final difference Fourier synthesis showed small residual electron density near the Zn and Br atoms, which can most likely be ascribed to the omission of absorption correction. The final values of the residuals were $R = 0.038$, $R_w = 0.050$ for 1987 significant reflections. Atomic positions and equivalent isotropic parameters of the non-hydrogen atoms are listed in Table 3. See also 'Supplementary Material'.

TABLE 2. Fractional atomic coordinates ($\times 10^4$) and equivalent isotropic temperature factors ($\times 100$) of the non-hydrogen atoms in CoL₂Cl₂^a

Atom	x/a	y/b	z/c	B_{iso}
Co	466.3(6)	730.6(3)	8699.1(4)	300.9(14)
Cl(1)	63(1)	-11(1)	7237(1)	419(3)
Cl(2)	-1320(1)	831(1)	9763(1)	440(3)
N(11)	429(4)	1475(2)	6485(3)	334(10)
N(21)	554(4)	1517(2)	7682(3)	313(9)
C(31)	853(5)	2123(2)	7936(3)	352(11)
C(41)	931(6)	2464(2)	6914(4)	401(13)
C(51)	656(5)	2029(2)	5986(3)	324(11)
C(31A)	1063(11)	2364(3)	9200(5)	56(2)
C(61)	613(5)	2111(2)	4713(3)	330(11)
C(71)	1436(6)	2608(2)	4365(4)	434(15)
C(81)	1394(7)	2696(3)	3175(5)	56(2)
C(91)	572(8)	2295(3)	2334(5)	58(2)
C(101)	-229(7)	1788(3)	2661(4)	53(2)
C(111)	-211(6)	1699(3)	3852(4)	430(14)
N(12)	2664(4)	762(2)	11140(3)	304(9)
N(22)	2519(4)	758(2)	9933(3)	301(9)
C(32)	3968(5)	812(2)	9780(3)	298(10)
C(42)	5034(5)	832(2)	10903(4)	346(11)
C(52)	4181(4)	799(2)	11749(3)	294(10)
C(32A)	4262(7)	843(3)	8567(4)	43(2)
C(62)	4677(4)	815(2)	13065(3)	285(10)
C(72)	3722(6)	1022(2)	13767(4)	420(14)
C(82)	4244(7)	1037(3)	15002(4)	51(2)
C(92)	5710(7)	831(2)	15547(4)	51(2)
C(102)	6685(7)	831(2)	14854(5)	501(15)
C(112)	6176(6)	612(2)	13621(4)	402(14)

^ae.s.d.s in the least significant digits are given in parentheses.

TABLE 3. Fractional atomic coordinates ($\times 10^4$) and equivalent isotropic temperature factors ($\times 10$) of the non-hydrogen atoms in ZnL₂Br₂^a

Atom	x/a	y/b	z/c	B_{iso}
Zn	388.5(8)	758.3(3)	8569.3(6)	30.1(2)
Br(1)	153.0(9)	-29.4(3)	7075.8(6)	42.0(2)
Br(2)	-1502.6(8)	831.6(3)	9617.7(7)	42.2(2)
N(11)	343(6)	1494(2)	6372(4)	33.0(14)
N(21)	469(7)	1544(2)	7558(4)	35.7(15)
C(31)	724(8)	2145(3)	7839(6)	38(2)
C(41)	732(9)	2478(3)	6795(5)	43(2)
C(51)	512(7)	2053(3)	5884(5)	33(2)
C(31A)	925(11)	2375(3)	9081(6)	56(3)
C(61)	422(8)	2130(3)	4600(5)	34(2)
C(71)	1224(9)	2607(3)	4244(6)	48(2)
C(81)	1179(12)	2696(4)	3042(7)	63(3)
C(91)	316(12)	2304(4)	2200(7)	62(3)
C(101)	-456(11)	1811(4)	2540(6)	59(3)
C(111)	-417(9)	1721(3)	3730(6)	44(2)
N(12)	2520(5)	809(2)	11040(4)	30.5(13)
N(22)	2403(6)	798(2)	9840(4)	30.0(14)
C(32)	3831(8)	813(3)	9728(6)	33(2)
C(42)	4881(8)	833(3)	10859(6)	37(2)
C(52)	4011(7)	822(3)	11678(5)	32(2)
C(32A)	4113(8)	836(3)	8508(6)	45(2)
C(62)	4504(8)	838(3)	13013(5)	34(2)
C(72)	3527(8)	1059(3)	13689(6)	40(2)
C(82)	4047(10)	1068(4)	14928(6)	54(2)
C(92)	5518(10)	871(4)	15507(7)	54(2)
C(102)	6449(9)	660(4)	14841(7)	53(2)
C(112)	5975(8)	641(3)	13609(6)	43(2)

^ae.s.d.s in the least significant digits are given in parentheses.

TABLE 4. Distorted tetrahedral compounds ML_2X_2 ($M = Co, Zn, Ni, Fe; X = Cl, Br$): colour, X-ray type, melting point and ligand field data^a

Compound	Colour	X-ray type	Melting point (°C)	Ligand field maxima ($\times 10^3 \text{ cm}^{-1}$)
$\alpha\text{-CoL}_2\text{Cl}_2$	blue	A	185	6.1; 7.2; 9.2; 16.3; 17.1
$\beta\text{-CoL}_2\text{Cl}_2$	blue	B	188	6.1; 7.2; 9.2; 16.3; 17.1
$\beta'\text{-CoL}_2\text{Br}_2$	blue	B'	196	6.0; 7.2; 9.1; 15.4; 16.0; 16.7
$\alpha\text{-ZnL}_2\text{Cl}_2$	white	A	180	(7.2; 9.2; 15.9)
$\beta\text{-ZnL}_2\text{Cl}_2$	white	B	189	
$\alpha'\text{-ZnL}_2\text{Br}_2$	white	A'	199	
$\beta'\text{-ZnL}_2\text{Br}_2$	white	B'	200	(7.3; 8.9; 15.2)
$\beta\text{-NiL}_2\text{Br}_2$	purple	B'	216	6.1; 10.5; 17.5
$\alpha'\text{-FeL}_2\text{Br}_2$	beige	A'	201	5.5

^aLigand field maxima in parentheses refer to 1% Co dopes in the isomorphous Zn compound.

Results and Discussion

General

Table 4 contains the colours, X-ray powder types, melting points and ligand field data of the compounds with 3-methyl-5-phenylpyrazole. Detailed powder diffraction data of $\beta\text{-ZnL}_2\text{Cl}_2$ and $\beta'\text{-ZnL}_2\text{Br}_2$ are listed in Table 5. Infrared spectral details are given in Table 6. The results of elemental analysis (metal, halogen, C, H, N) are satisfactory, see 'Supplementary Material'.

The infrared spectral data and the X-ray powder patterns indicate that two types of compounds are found for the chlorides, called α and β , and two for the bromides, called α' and β' . The X-ray patterns are isotypical for α and α' and β and β' , respectively, indicating similar structures.

The ligand field spectra (Table 4) clearly indicate that the coordination geometry for M^{2+} is tetrahedral with a $[\text{MN}_2\text{X}_2]$ chromophore [9]. For $\alpha\text{-CoL}_2\text{Cl}_2$ and $\beta\text{-CoL}_2\text{Cl}_2$ identical ligand field spectra are found, suggesting very similar coordination geometries for the α - and β -modification.

It was observed during a very large number of experimental trials, that when both isomers are

TABLE 5. Powder diffraction data for $\alpha\text{-ZnL}_2\text{Cl}_2$, $\alpha'\text{-ZnL}_2\text{Br}_2$, $\beta\text{-ZnL}_2\text{Cl}_2$ and $\beta'\text{-ZnL}_2\text{Br}_2$

d (Å)	I/I_0 (%)	d (Å)	I/I_0 (%)
$\alpha\text{-ZnL}_2\text{Cl}_2$		$\alpha'\text{-ZnL}_2\text{Br}_2$	
7.196	100	7.550	16
5.616	30	6.692	100
5.056	14	5.366	20
4.840	17	4.768	26
4.740	14	4.666	20
4.690	25	3.978	28
3.878	22	3.604	45
3.667	19	3.551	25
3.616	19	3.353	31
3.336	54	3.211	22
$\beta\text{-ZnL}_2\text{Cl}_2$		$\beta'\text{-ZnL}_2\text{Br}_2$	
7.899	10	8.067	57
6.223	6	6.748	6
5.269	16	5.877	5
5.231	27	4.372	100
4.260	18	3.831	37
3.950	22	3.707	20
3.757	16	3.525	70
3.698	10		
3.636	7		
3.504	100		

TABLE 6. Infrared spectral data for $\alpha\text{-ZnL}_2\text{Cl}_2$, $\beta\text{-ZnL}_2\text{Cl}_2$, $\alpha'\text{-ZnL}_2\text{Br}_2$ and $\beta'\text{-ZnL}_2\text{Br}_2$ ^a

Compound	ν_{NH}	γ_{NH}	Remaining characteristic ligand vibrations
$\alpha\text{-ZnL}_2\text{Cl}_2$	3305(s)	815(s)	1565, 1495, 1460(b), 1300, 1275–1265(d), 1210–1195(d), 1155, 1045, 765, 725, 690, 670, 620–610(d), 570, 515
$\beta\text{-ZnL}_2\text{Cl}_2$	3330–3360(d)	810–825(d)	1565, 1495, 1460(b), 1295, 1270(s), 1200(s), 1185–1155(t), 1040, 765, 725, 690, 665, 620(s), 580, 510
$\alpha'\text{-ZnL}_2\text{Br}_2$	3335(s)	810–820(d)	1565, 1495, 1460(b), 1295, 1270(s), 1210–1200(d), 1180–1160, 1045, 765, 720, 690, 660, 615(s), 585–560(d), 515
$\beta'\text{-ZnL}_2\text{Br}_2$	3340(s)	810–820(d)	1565, 1495, 1460(b), 1295, 1270(s), 1200(s), 1175–1155(d), 1050–1040(d), 765, 720, 690, 665, 620(s), 575, 510

^aSmall differences exist between the spectra of the compounds of the same modification but with different $M(\text{II})$ ions; b = ligand + nujol vibration, s = singlet, d = doublet, t = triplet.

formed, the α isomer precipitates first, whereas the β isomer crystallizes from the mother liquor. The β isomers β -CoL₂Cl₂ and β' -ZnL₂Br₂ yielded crystals suitable for single crystal analyses. α' -FeL₂Br₂ also yielded crystals which, unfortunately, were found to be unsuitable for single-crystal X-ray analysis.

The crystal structures of two representative examples, i.e. β -CoL₂Cl₂ and β' -ZnL₂Br₂, are described below.

Description of the Structures

The monomeric units of β -CoL₂Cl₂ and β' -ZnL₂Br₂ are shown in Fig. 1, together with the atomic labeling scheme used. Relevant bond lengths and angles are listed in Table 7. Bond distances and angles within the ligands are normal, see 'Supplementary Material'.

In both compounds the ligand occurs only as the 3-methyl-5-phenylpyrazole tautomer. The metal ions are tetrahedrally coordinated by two pyrazole nitrogen atoms and two halide anions; the metal–nitrogen and metal–halogen distances observed are not uncommon. From Table 7, it is clear that the tetrahedra are severely distorted: the angles Cl(1)–Co–Cl(2) and Cl(1)–Co–N(22) are 118.12(5) and 119.9(1)°, respectively, whereas the corresponding angles Br(1)–Zn–Br(2) and Br(1)–Zn–N(22) are 118.89(4) and 116.6(1)°. The angles Cl(1)–Co–N(21), N(21)–Co–N(22), Br(1)–Zn–N(21) and N(21)–Zn–N(22) are 98.6(1)°, 103.3(1)°, 100.1(1)° and 102.5(2)°, respectively, small compared to normal tetrahedral angles. The arrangement of the molecules in the unit cell is shown in Fig. 2;

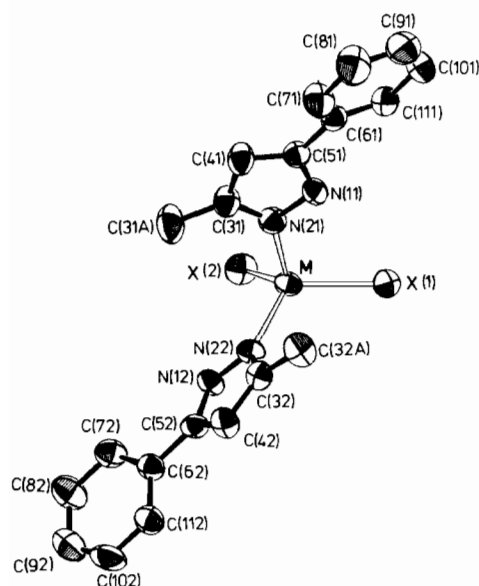


Fig. 1. ORTEP drawing of the monomeric units of dichlorobis(3-methyl-5-phenylpyrazole)cobalt(II) (M = Co and X = Cl) and dibromobis(3-methyl-5-phenylpyrazole)zinc(II) (M = Zn and X = Br).

TABLE 7. Selected coordination bond distances (Å) and bond angles (°) for β -CoL₂Cl₂ and β' -ZnL₂Br₂

Atoms	Distance
β -CoL ₂ Cl ₂	
Co–Cl(1)	2.252(1)
Co–Cl(2)	2.222(1)
Co–N(21)	2.031(3)
Co–N(22)	2.008(3)
β' -ZnL ₂ Br ₂	
Zn–Br(1)	2.373(1)
Zn–Br(2)	2.345(1)
Zn–N(21)	2.053(5)
Zn–N(22)	2.013(5)
Atoms	Angle
β -CoL ₂ Cl ₂	
Cl(1)–Co–Cl(2)	118.12(5)
Cl(1)–Co–N(21)	98.6(1)
Cl(1)–Co–N(22)	119.9(1)
Cl(2)–Co–N(21)	111.06(9)
Cl(2)–Co–N(22)	104.06(9)
N(21)–Co–N(22)	103.3(1)
β' -ZnL ₂ Br ₂	
Br(1)–Zn–Br(2)	118.89(4)
Br(1)–Zn–N(21)	100.1(1)
Br(1)–Zn–N(22)	116.6(1)
Br(2)–Zn–N(21)	112.2(2)
Br(2)–Zn–N(22)	105.4(1)
N(21)–Zn–N(22)	102.5(2)

the crystal packing of the two compounds is very similar. Table 8 contains relevant intermolecular distances and angles (including hydrogen bonding data) in β -CoL₂Cl₂ and β' -ZnL₂Br₂. Remarkable is the pairwise arrangement of monomers, with metal–metal closest distances of 4.490(1) Å for M = Co and 4.801(1) Å for M = Zn. In fact, the structures can almost be regarded as consisting of asymmetrical halide-bridged dimers, in which the coordination geometry of the metal ions is almost trigonal bipyramidal (the angles N(21)–Co–Cl(2)' and N(21)–Zn–Br(2)' are 163.3(1) and 162.5(2)°, respectively). The distances Co...Cl(2)' = 3.704(1) Å and Zn...Br(2)' = 3.969(1) Å, however, are considered too long for bonding distances (compare Co–Cl(2) = 2.222(1) Å and Zn–Br(2) = 2.345(1) Å for the tetrahedral bond lengths).

From Table 8, it is clear that hydrogen bonding interactions are rather weak. Only the interactions involving H(11) can be considered significant (H(11)...Cl(1) = 2.70(4) Å, H(11)...Br(1) = 2.700(5) Å). The corresponding N(11)...X(1) distances are 3.264(4) Å for β -CoL₂Cl₂ and 3.364(5) Å for β' -ZnL₂Br₂. The distances H(12)...X(2) and H(12)...X(1)' (X = Cl, Br), however, are probably sufficiently close to the sum of the van der Waals radii to warrant

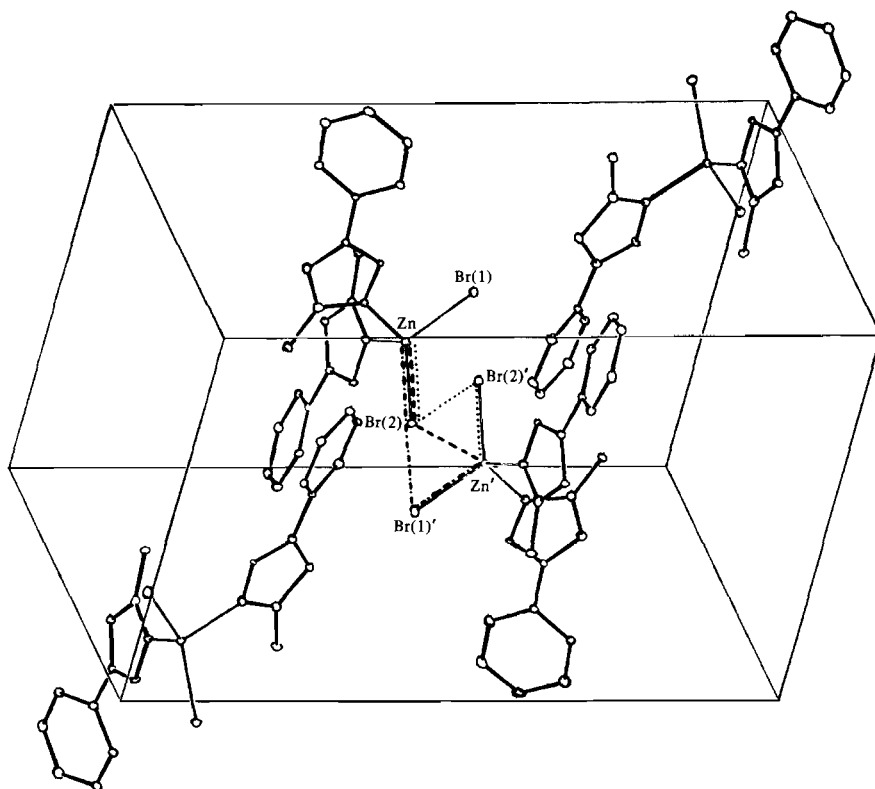


Fig. 2. ORTEP drawing of the unit cell of dibromobis(3-methyl-5-phenylpyrazole)zinc(II). Possible magnetic interaction pathways in the isomorphous compound dibromobis(3-methyl-5-phenylpyrazole)cobalt(II) are represented by: ---- = pathway 1, = pathway 2, - · - = pathway 3.

TABLE 8. Relevant intermolecular distances (Å) and hydrogen bonding data and intermolecular angles (°) for β -CoL₂Cl₂ and β -ZnL₂Br₂

Atoms	Distance
β -CoL ₂ Cl ₂	
Co...Co'	4.490(1)
Co...Cl(2)'	3.704(1)
Cl(1)...Cl(2)'	3.770(2)
Cl(2)...Cl(2)'	4.143(2)
H(12)...Cl(1)'	2.89(4)
N(12)...Cl(1)'	3.725(4)
H(11)...Cl(1)	2.70(4)
N(11)...Cl(1)	3.264(4)
H(12)...Cl(2)	2.93(4)
N(12)...Cl(2)	3.480(3)
β -ZnL ₂ Br ₂	
Zn...Zn'	4.801(1)
Zn...Br(2)'	3.969(1)
Br(1)...Br(2)'	4.057(1)
Br(2)...Br(2)'	4.412(1)
H(12)...Br(1)'	3.087(5)
N(12)...Br(1)'	4.013(5)
H(11)...Br(1)	2.700(5)
N(11)...Br(1)	3.364(5)

(continued)

TABLE 8. (continued)

Atoms	Distance
H(12)...Br(2)	2.990(5)
N(12)...Br(2)	3.570(5)
Atoms	Angles
β -CoL ₂ Cl ₂	
Cl(1)-Co...Cl(2)'	74.08(4)
Cl(2)-Co...Cl(2)'	84.78(4)
N(21)-Co...Cl(2)'	163.3(1)
N(22)-Co...Cl(2)'	69.19(9)
Co-Cl(2)...Co'	95.22(4)
Co-Cl(2)...Cl(2)'	62.93(3)
Co-Cl(1)...Cl(2)'	70.86(3)
N(12)-H(12)...Cl(1)'	155(3)
N(11)-H(11)...Cl(1)	131(3)
N(12)-H(12)...Cl(2)	121(3)
β -ZnL ₂ Br ₂	
Br(1)-Zn...Br(2)'	74.83(3)
Br(2)-Zn...Br(2)'	84.47(3)
N(21)-Zn...Br(2)'	162.5(2)
N(22)-Zn...Br(2)'	66.4(1)
Zn-Br(2)...Zn'	95.53(3)

(continued)

TABLE 8. (continued)

Atoms	Angles
Zn–Br(2)···Br(2)'	63.58(2)
Zn–Br(1)···Br(2)'	70.79(2)
N(12)–H(12)···Br(1)'	144.21(9)
N(11)–H(11)···Br(1)	119.3(1)
N(12)–H(12)···Br(2)	114.12(4)

consideration as a bifurcated hydrogen bonding interaction, albeit a weak one. Further evidence for the presence of weak hydrogen bonding is given by the positions of the $\nu(\text{NH})$ vibration in the IR spectra (3345 and 3340 cm^{-1} for $\beta\text{-CoL}_2\text{Cl}_2$ and $\beta'\text{-ZnL}_2\text{Br}_2$, respectively).

Theazole and phenyl rings of the ligands are planar; for least-squares planes and distances of the ring atoms to the best planes see 'Supplementary Material'. In $\beta\text{-CoL}_2\text{Cl}_2$, the phenyl groups of the ligands make angles with theazole rings of 24.7(2) and 25.7(2) $^\circ$; the corresponding angles in $\beta'\text{-ZnL}_2\text{Br}_2$ are 28.0(3) and 23.0(3) $^\circ$, respectively. Stacking of ligand rings in the structures is not observed.

Magnetic Susceptibility Measurements

Because of the observed $\text{M}\cdots\text{M}$ contacts below 5 Å, the Co, Ni and Fe compounds were studied by magnetic susceptibility measurements down to 4 K. The results, given in Table 9, indicate that only weak magnetic interaction exists between the paramagnetic metal ions in these compounds. The temperature dependence of the molar magnetic susceptibility χ_{M} for $\beta'\text{-CoL}_2\text{Br}_2$ shows a maximum at 6 K, indicating weak magnetic exchange between the Co ions. As the single crystal structures of $\beta\text{-CoL}_2\text{Cl}_2$ and $\beta'\text{-ZnL}_2\text{Br}_2$ contain relatively short intermolecular $\text{M}\cdots\text{X}$ and $\text{X}\cdots\text{X}$ distances, it might be possible to describe the magnetic exchange interactions in the Co compounds by expressions for the exchange in Co dimers. Therefore, it was tried to fit the susceptibility data of the Co compounds to the Heisenberg [10] (eqn. (1)) and Ising [11] (eqn. (2)) Hamiltonians for Co(II) dimers, respectively.

$$\chi = \frac{Ng^2\beta^2}{kT} \times \frac{1}{3 + e^{-2x}} \quad (1)$$

$$\chi = \frac{Ng^2\beta^2}{kT} \times \frac{1}{6 + 6e^{-x}} \quad (2)$$

($x = J/kT$)

For all compounds the magnetic data do not fit satisfactorily to the equations given here at temperatures above 10 K. Therefore, the calculated values for the exchange constant J and the spectroscopic splitting constant g are not given here.

TABLE 9. Data from the magnetic susceptibility measurements

Compound	θ (K) ^a	$\mu_{\text{eff}}(40 \text{ K})$ (BM)
$\alpha\text{-CoL}_2\text{Cl}_2$	–4	4.4
$\beta\text{-CoL}_2\text{Cl}_2$	–10	4.4
$\beta'\text{-CoL}_2\text{Br}_2$		4.2
$\alpha'\text{-FeL}_2\text{Br}_2$	5	7.2
$\beta'\text{-NiL}_2\text{Br}_2$	3	3.6

^aObtained from $1/\chi$ vs. T .

There are at least three possible pathways for the exchange interactions between the metal centres in these compounds. First, the p or low-lying d orbitals of the asymmetrically 'bridging' halide ions may be involved (pathway 1 in Fig. 2), causing magnetic exchange between the metal ions in adjacent monomers. Another possibility is 'double-halide exchange' [12–16] via X(2) and X(2)' or via X(2) and X(1)' (corresponding to pathways 2 and 3 in Fig. 2, respectively). Relevant intermolecular distances and angles are given in Table 8, showing that the shortest halide–halide contacts occur for X(1) of one monomer and X(2) of the adjacent molecule. The internuclear separations are 3.770 Å in $\beta\text{-CoL}_2\text{Cl}_2$ and 4.057 Å in $\beta'\text{-ZnL}_2\text{Br}_2$. This observation suggests that pathway 3 is the more likely one.

Hatfield and Jones [13] reported the magnetic properties of $[\text{Co}(\text{NH}_3)_6][\text{CuCl}_5]$, which show an antiferromagnetic transition at 8 K, suggesting weak spin coupling. This observation agrees with the weak spin coupling in the case of cation–anion–anion–cation interaction in the presence of half-filled σ -orbitals [12]. The Cl–Cl distances between the axial chloride of one CuCl_5^{3-} ion and the axial chloride ligands of three adjacent CuCl_5^{3-} units in the corresponding Cr(III) compound $[\text{Cr}(\text{NH}_3)_6][\text{CuCl}_5]$ are 4.11 Å and the Cu–Cl–Cl' angles are 144.74 $^\circ$. Brown *et al.* [14] published a series of polymeric adenine complexes having the general formula $(\text{AdH}^+)_2\text{CuX}_4$ (AdH^+ = protonated adenine). In the Cl and Br compounds the monomeric units are linked into zigzag chains with halide–halide distances of 3.775 Å for the Cl compound and 3.791 Å for the Br adduct. The Cu–Cl···Cl angle was calculated to be 169.23 $^\circ$. The weak magnetic exchange in these compounds was ascribed to double-halide interaction. These examples show that the halide–halide distances in the present compounds are possibly adequate to provide a pathway for magnetic exchange. However, the M–X(1)–X(2)' angles, calculated to be 70.86 $^\circ$ in $\beta\text{-CoL}_2\text{Cl}_2$ and 70.79 $^\circ$ in $\beta'\text{-ZnL}_2\text{Br}_2$, are clearly too small to allow double-halide exchange [14]. Further magnetic investigations are needed to provide concluding evidence for one of the mechanisms.

Discussion on the Occurrence of Isomers

The structural differences between the two isomeric modifications for the Co and Zn compounds can have several origins. First, two different coordination modes of 3(5)-methyl-5(3)-phenylpyrazole may be involved. Banditelli *et al.* [17, 18] found that the two methyl signals in the ^1H NMR spectrum of AuL_2Cl originated from two coordination modes of the ligand (coordination via different N atoms). In the solution ^1H NMR spectra of the Zn isomers reported here the methyl signals were found at the same position (2.28 ppm (CDCl_3)) in the Cl and Br compounds). This observation, however, does not necessarily disagree with the existence of different coordination modes as the ligand exchange for Zn(II) compounds is supposed to be fast on the NMR time scale. Alternatively, the isomers may be crystal modifications with difference in crystal packings of the monomers [19, 20]. This phenomenon would agree with the absence of (strong) hydrogen bonding. Graves *et al.* [19] found even four crystal modifications of *cis*- $\text{PtCl}_2(\text{NMIz})_2$ and van Ooijen [20] found $\text{CuCl}_2(\text{NMIz})_2$ to yield two modifications. The X-ray powder patterns and the IR spectra of the modifications are clearly different. The ligand field spectra of the modifications of $\text{CuCl}_2(\text{NMIz})_2$ are very similar, which was already anticipated as the same donor atoms bind to copper in both cases. The similarities between the results presented in this paper (see 'General') and those published by Graves *et al.* [19] and van Ooijen [20], suggest only a difference in crystal packing for the Co and Zn compounds. This also agrees with the observation that the melting points of the modifications are nearly identical.

Conclusions

A series of compounds with the general formula ML_2X_2 yielded different crystal modifications of the chlorides and bromides of the Co and Zn compounds. The crystal structures of two representative examples, i.e. β - CoL_2Cl_2 and β' - ZnL_2Br_2 , were found to be very similar. Both structures can be described as consisting of pseudo-tetrahedral monomeric units, which are arranged in pairs with remarkably short intermolecular metal-halide and halide-halide distances. The paramagnetic compounds showed weak magnetic exchange between the metal ions. The exchange pathway, responsible for this behaviour, is not known yet.

Supplementary Material

Listings of observed and calculated structure factors, hydrogen atom positions, anisotropic thermal parameters of the non-hydrogen atoms, elemental analyses, bond distances and angles within the ligands and least-squares planes and distances of the ring atoms to the best planes are available from the authors on request.

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