# Cyanato–Copper(II) Complexes with Organic Ligands [1]. XXI. Effect of Imidazole Ligands on the Structure Properties of Cyanato–Copper(II) Complexes*

A. MAŠLEJOVÁ, J. KOHOUT and J. GAŽO

*Department of Inorganic Chemistry, Slovak Technical University, 812 37 Bratislava, Czechoslovakia*

Received February 4, 1982

*Compounds of the type $Cu(NCO)_2L_2$ were prepared, where L was imidazole, 1- or 2-methyl-, 2-ethyl-, 1,2-dimethylimidazole, 2-methyl- and 2-ethylbenzimidazole. The results of physical methods show that these complexes have elongated octahedral stereochemistries with various degree of axial interaction or five coordinate arrangement. The weaker axial bondings of the Cu(II) atom are realized by free oxygens or – in two cases – by equatorially bonded nitrogens of the NCO groups. Two isomers of $Cu(NCO)_2(2\text{-ethylbenzimidazole})_2$ were isolated, in which the various degree of axial distortion is associated with such a different axial ligation.*

## Introduction

Metal complexes of imidazole ligands [2] were studied by X-ray crystallography and by various physical methods. The compound $CuCl_2(iz)_2$ exhibits (according to the X-ray results [3]) a five-coordinate, tetragonal pyramidal configuration. Further, the compounds $CuCl_2(iz)_4$ [4], $CuX_2(bz)_4$ (X = Cl, Br) [5] and $CuCl_2(2\text{-meiz})_4$ [6] were prepared, for which tetragonal octahedral stereochemistries were claimed. On the other hand, for the 1:2 complexes $CuX_2(2\text{-meiz})_2$ (X = Cl, Br) [6, 7] a distorted tetrahedral arrangement was postulated. This paper presents the physical properties of cyanato–copper(II) complexes with imidazole and its derivatives and characterizes their structural features. The analogous thiocyanato–copper(II) complexes will be reported elsewhere [8].

## Experimental

### Chemicals

Imidazole, 1- or 2-methyl-, 2-ethyl-, 1,2-dimethylimidazole (Fluka) were used without further purification. 2-methyl- and 2-ethylbenzimidazole were synthesized by the method of Phillips [9].

### Preparation

*$Cu(NCO)_2L_2$, where L = iz, 1-meiz, 2-meiz, 2-etiz, 1,2-dimeiz, 2-mebz*

Aqueous solution of $Cu(NO_3)_2 \cdot 3H_2O$ was mixed with aqueous solution of KNCO and was added to an aqueous or methanolic solution of the ligand L. The solutions were left to crystallize in a refrigerator. The crystalline precipitates were sucked off, washed with water and dried in a desiccator over KOH.

*α-$Cu(NCO)_2(2\text{-etbz})_2$*

Aqueous solution of $Cu(NO_3)_2 \cdot 3H_2O$ was poured together with aqueous solution of KNCO, and this was added to methanolic solution of 2-etbz. The temperature of the solutions was 35 °C. The crystalline precipitate was formed by standing and slow cooling of the reaction system. The product was sucked off, washed with water and dried in a desiccator over KOH.

*β-$Cu(NCO)_2(2\text{-etbz})_2$*

The preparation procedure was the same as for the α-isomer, but the temperature of the solutions was 15 °C. The obtained system had to be intensively cooled by water with ice.

*Solutions used*

1. 25 mmol of $Cu(NO_3)_2 \cdot 3H_2O$ in 50 $cm^3$ of water, 53 mmol of KNCO in 50 $cm^3$ of water and 55 mmol of iz or 2-mebz in 100 $cm^3$ of methanol; 2. 25 mmol of $Cu(NO_3)_2 \cdot 3H_2O$ in 50 $cm^3$ of water, 53 mmol of KNCO in 50 $cm^3$ of water and 56 mmol of 1- or 2-meiz, 2-etiz or 1,2-dimeiz in 50 $cm^3$ of water; 3. 4 mmol of $Cu(NO_3)_2 \cdot 3H_2O$ in 25 $cm^3$ of water, 8.6 mmol of KNCO in 25 $cm^3$ of water and 10.2 mmol of 2-etbz in 50 $cm^3$ of methanol.

All attempts to prepare a complex of the composition $Cu(NCO)_2(bz)_2$ led to products contaminated

---

*Dedicated to Professor J. Klikorka on the occasion of his 60th birthday.

0020-1693/82/0000-0000/$02.75

TABLE I. Analytical Data.

| Compound | Colour | Calc. (%)<br>Found (%) | | | |
|---|---|---|---|---|---|
| | | C | H | N | Cu |
| Cu(NCO)$_2$(iz)$_2$ | Light blue | 33.86 | 2.84 | 29.62 | 22.40 |
| | | 33.10 | 2.83 | 29.60 | 22.40 |
| Cu(NCO)$_2$(1-meiz)$_2$ | Light blue-violet | 38.52 | 3.88 | 26.95 | 20.38 |
| | | 38.50 | 3.90 | 26.89 | 20.45 |
| Cu(NCO)$_2$(2-meiz)$_2$ | Violet-blue | 38.52 | 3.88 | 26.95 | 20.38 |
| | | 38.12 | 3.82 | 26.80 | 20.40 |
| Cu(NCO)$_2$(2-etiz)$_2$ | Blue | 42.41 | 4.75 | 24.73 | 18.70 |
| | | 41.78 | 4.75 | 24.53 | 18.78 |
| Cu(NCO)$_2$(1,2-dimeiz)$_2$ | Navy blue | 42.41 | 4.75 | 24.73 | 18.70 |
| | | 41.81 | 4.70 | 24.53 | 18.72 |
| Cu(NCO)$_2$(2-mebz)$_2$ | Grey-violet | 52.44 | 3.91 | 20.39 | 15.42 |
| | | 52.31 | 3.97 | 20.36 | 15.40 |
| $\alpha$-Cu(NCO)$_2$(2-etbz)$_2$ | Deep violet | 54.60 | 4.58 | 19.10 | 14.44 |
| | | 54.30 | 4.55 | 19.16 | 14.46 |
| $\beta$-Cu(NCO)$_2$(2-etbz)$_2$ | Deep green | 54.60 | 4.58 | 19.10 | 14.44 |
| | | 54.70 | 4.60 | 19.13 | 14.49 |

TABLE II. Cyanate and Copper–Nitrogen Vibrations (cm$^{-1}$).[a]

| Complex | $\nu_{as}$ (NCO) | $\nu_s$ (NCO) | $\delta$(NCO) | $\nu$(Cu–NCO) | $\nu$(Cu–N(L)) |
|---|---|---|---|---|---|
| Cu(NCO)$_2$(iz)$_2$ | 2236 vs | [b] | 607 s | 357 s | 291 s, 269 ms |
| Cu(NCO)$_2$(1-meiz)$_2$ | 2228 vs, 2198 vs | 1331 m | 615 s | 364 s | 296 ms, 282 sh |
| Cu(NCO)$_2$(2-meiz)$_2$ | 2231 vs, 2201 vs | 1327 sh, 1321 m | 637 mw, 610 s | 357 s | 297 ms |
| Cu(NCO)$_2$(2-etiz)$_2$ | 2186 vs | [b] | 608 s | 369 s | 253 m |
| Cu(NCO)$_2$(1,2-dimeiz)$_2$ | 2231 vs, 2198 vs | 1327 m | 614 s | 354 vs[d] | 273 s |
| Cu(NCO)$_2$(2-mebz)$_2$ | 2227 vs | 1349 m, 1317 m | 614 s, 606 s | 379 vs[d] | 253 s |
| $\alpha$-Cu(NCO)$_2$(2-etbz)$_2$ | 2212 vs | 1327 ms | 612 ms[c], 595 s[c] | 380 vs[d] | 276 s[c,d] |
| $\beta$-Cu(NCO)$_2$(2-etbz)$_2$ | 2232 vs, 2206 vs | 1343 m | 649 m, 607 s[c]<br>597 s[c] | 383 vs[d] | 258 ms |

[a] s = strong, m = medium, w = weak, sh = shoulder, v = very. [b] Overlapped by the L ligand bands. [c] Cannot be identified with certainty due to the presence of L ligand bands. [d] A very weak splitting occurs.

by red bis(benzimidazolate) copper(II), described already by Goodgame and Haines [5].

The violet and green crystals of $\alpha$- and $\beta$-Cu(NCO)$_2$(2-etbz)$_2$ are very different: their X-ray diffraction patterns (Fig. 1) show almost no common features.

### *Analysis*

Elemental analyses were carried out on a C, H, N, Analyser (Carlo Erba). Copper was determined by chelatometric titration. The analytical and other basic data are summarized in Table I.

### *Physical Measurements*

The infrared [10], solid state electronic [10] and ESR-spectra [11], as well as the room temperature magnetic susceptibilities [10], were obtained as described in the cited papers. The temperature dependence of the magnetic susceptibility for $\alpha$- and $\beta$-Cu(NCO)$_2$(2-etbz)$_2$ was measured as in [12].

## Results and Discussion

### *Infrared Spectra*

The infrared bands belonging to the cyanate and copper–nitrogen vibrations were identified by comparison with published spectra [13] of the pure ligands, as well as of the corresponding Cu(NCS)$_2$L$_2$ complexes [8]. The frequencies of these vibrations are given in Table II.

TABLE III. ESR and Electronic Spectral Data and Magnetic Moments (20 °C).

| Complex | $g_{\parallel}$ | $g_{\perp}$ | G | $\tilde{\nu}_{max}$ ($10^3$ cm$^{-1}$)[d] | $\mu_{eff}$ (B.M.) |
|---|---|---|---|---|---|
| $Cu(NCO)_2(iz)_2$ | 2.251 | 2.040 | 6.28 | 15.5 | 1.83 |
| $Cu(NCO)_2$(1-meiz)$_2$ | 2.237 | 2.059 | 4.02 | 15.1 ≈18.0 sh | 1.87 |
| $Cu(NCO)_2$(2-meiz)$_2$ | 2.272 | 2.073 | 3.73 | 16.3 | 1.87 |
| $Cu(NCO)_2$(2-etiz)$_2$ | 2.274 | 2.046 | 5.96 | 14.0 ≈17.3 sh | 1.88 |
| $Cu(NCO)_2$(1,2-dimeiz)$_2$ | 2.300 | 2.063 | 4.76 | 15.6 | 1.87 |
| $Cu(NCO)_2$(2-mebz)$_2$ | 2.06[a] | | | 17.6 | 1.83 |
| α-$Cu(NCO)_2$(2-etbz)$_2$ | 2.227 | 2.042 | 5.40 | ≈14.4 sh 18.8 | 1.82 |
| β-$Cu(NCO)_2$(2-etbz)$_2$ | 2.178[b] | 2.054[c] | | 16.1 | 1.85 |

[a] The $g_0$ value from the pseudoisotropic ESR spectrum. [b] The value determined at the maximum and [c] minimum of the derivative curve. [d] sh = shoulder.

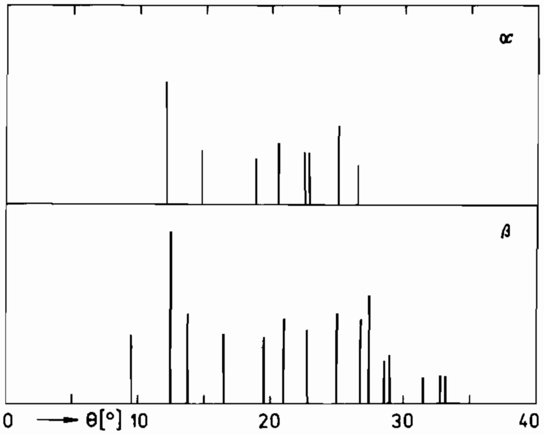

Fig. 1. X-ray diffraction patterns of α- and β-$Cu(NCO)_2$-(2-etbz)$_2$.

### Cyanate vibrations

All studied complexes exhibit the $\nu_{as}$(NCO) vibrations in the range of *ca.* 2235–2185 cm$^{-1}$, with a doublet splitting observed in some cases, and the $\nu_s$(NCO) modes in the range of *ca.* 1350–1315 cm$^{-1}$. The deformation NCO modes appear between ≈650–595 cm$^{-1}$; they are mostly single or split into a doublet by as much as 17 cm$^{-1}$. These results suggest [14] terminal nitrogen bonded NCO groups, possibly involved in pseudobridges through their oxygen atoms [15]. As was pointed out [14], such type of NCO group pseudobridging cannot be determined from the behaviour of the δ(NCO) mode. For $Cu(NCO)_2$(2-meiz)$_2$ the δ(NCO) mode shows a splitting by 27 cm$^{-1}$ and consequently N-pseudobridging NCO groups may be admitted. The compound β-$Cu(NCO)_2$(2-etbz)$_2$ has this mode probably split into three components in the range of 52 cm$^{-1}$, so that the presence of cyanate N-bridges is indicated [14].

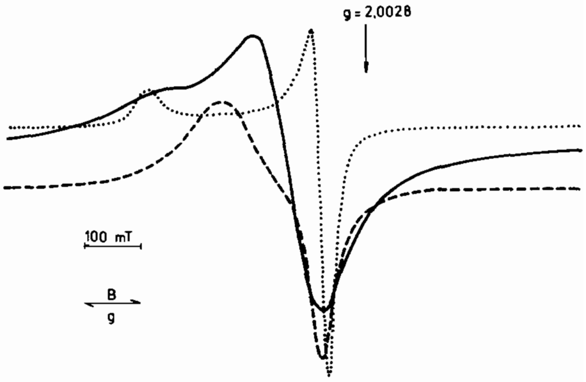

Fig. 2. ESR spectra of $Cu(NCO)_2$(2-meiz)$_2$ (——), $Cu(NCO)_2$(2-etiz)$_2$ (·····), and β-$Cu(NCO)_2$(2-etbz)$_2$ (-----).

### Copper–nitrogen vibrations

The strong bands in the region of *ca.* 380–355 cm$^{-1}$ can be assigned [14, 16] to the ν(Cu–NCO) stretching vibrations, while the medium to strong bands in the range of *ca.* 295–255 cm$^{-1}$ can be attributed [17] to the ν(Cu–N(L)) stretching vibrations. For the complexes of iz and 1-meiz these latter vibrations are split by as much as ≈20 cm$^{-1}$.

The complexes of 2-mebz and 2-etbz have their ν(Cu–NCO) frequencies higher by about 20 cm$^{-1}$ than those of alkylimidazoles and the ν(Cu–N(L)) frequencies are usually lower (though they are rather variable). This is a similar phenomenon as observed in the case of cyanato–copper(II) complexes with methylpyridines [16]. According to the ν(Cu–N(L)) values, $Cu(NCO)_2(iz)_2$ when compared with $Cu(NCO)_2(iz)_2$ shows a considerable weakening of the Cu–N(L) bonds; similar weakening, though to a smaller degree, appears for $Cu(NCO)_2$(1,2-dimeiz)$_2$.

The isomers of $Cu(NCO)_2$(2-etbz)$_2$ strongly differ in their ν(Cu–N(L)) value, which is for the α-isomer higher by ≈20 cm$^{-1}$ (the ν(Cu–NCO) values being very close). Assigning tetragonal structures to both compounds, this fact may reveal a greater tetragonal distortion for the α-isomer, which results in total strengthening of the equatorial bonds [18].

*ESR Spectra*

The ESR spectra of the complexes under investigation (Table III, Fig. 2), except for $Cu(NCO)_2(2\text{-mebz})_2$, are of axial type; the spectrum of β-$Cu(NCO)_2(2\text{-etbz})_2$ is strongly affected by exchange coupling [19]. The $Cu(NCO)_2(2\text{-mebz})_2$ shows a pseudoisotropic spectrum, having on its broad asymmetric line the g value unresolved, so that only the $g_0$ value at the inflection point can be determined [20].

The $g_\parallel$ values occur in the range of *ca.* 2.24–2.30 and the $g_\perp$ values, corrected for the Gaussian line shape [21], in the range of *ca.* 2.04–2.07. Since the values of $G = (g_\parallel - 2)/(g_\perp - 2)$ in general are greater than 4, these g values correctly predict the Cu(II) atom ground state, being $d_{x^2-y^2}$ [19]. Only for $Cu(NCO)_2(2\text{-meiz})_2$ is the G value below 4, suggesting (in agreement with the line shape about $g_\parallel$) some exchange coupling between the weakly bridged Cu(II) atoms.

The high $g_\parallel$ values for complexes of 2-meiz, 2-etiz and 1,2-dimeiz indicate their pseudooctahedral or five coordinate stereochemistries. In these cases the equatorial bonds are weakened compared with the pronounced tetragonal system and thus, the $g_\parallel$ values should increase [22]. On the other hand, $Cu(NCO)_2(1\text{-meiz})_2$ and α-$Cu(NCO)_2(2\text{-etbz})_2$ exhibit the lowest $g_\parallel$ values, suggesting the strong tetragonal distortion in these complexes.

The feature of the ESR spectrum of β-$Cu(NCO)_2(2\text{-etbz})_2$ is consistent with a significant axial interaction, which makes possible an exchange coupling between magnetically unequivalent Cu(II) atoms [19].

*Electronic Spectra*

The ligand field spectral data are listed in Table III; some of the spectra are exemplified in Fig. 3.

The complexes with L = iz, 2-meiz, 1,2-dimeiz and 2-mebz, as well as β-$Cu(NCO)_2(2\text{-etbz})_2$ exhibit a single $d \leftarrow d$ band with its maximum in the range of 15500–17600 $cm^{-1}$. This band is for $Cu(NCO)_2(2\text{-meiz})_2$ fairly symmetric, for $Cu(NCO)_2(1,2\text{-dimeiz})_2$ it is broader, and for complexes of iz, 2-mebz, and for β-$Cu(NCO)_2(2\text{-etbz})_2$ it is perceptibly asymmetric on the low wavenumber side. Taking together our data on the position and shape of the $d \leftarrow d$ bands, it seems reasonable [19a, 23] to attribute pseudooctahedral structures to the complexes of 2-meiz and 1,2-dimeiz, supported by the $g_\parallel$ values. The remaining complexes have apparently stronger tetragonal arrangements, especially $Cu(NCO)_2(2\text{-mebz})_2$ in respect of its high band maxima wavenumber.

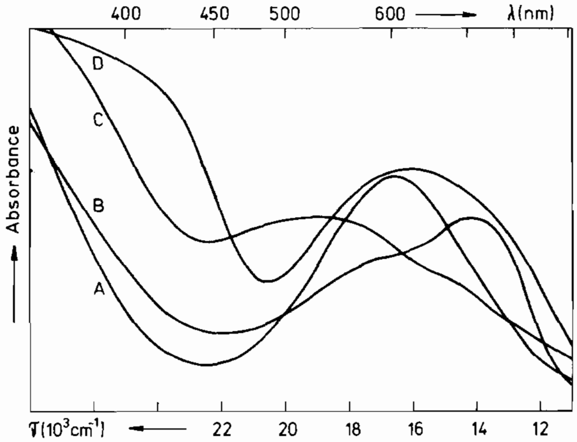

Fig. 3. Ligand field spectra of A – $Cu(NCO)_2(2\text{-meiz})_2$, B – $Cu(NCO)_2(2\text{-etiz})_2$, C – α-$Cu(NCO)_2(2\text{-etbz})_2$, and D – β-$Cu(NCO)_2(2\text{-etbz})_2$.

In all probability, the structures of these compounds are formed by basic units of the type *trans*-$CuN_2(2NCO)N_2(2L)$. From analogy with the finding of papers [3, 24] we assume that imidazole ligands are bonded by a tertiary nitrogen atom. The completion of the planar units to the elongated octahedra can be realized [14] through cyanate oxygen or nitrogen atoms from the adjacent units. In complexes of iz, 1,2-dimeiz and 2-mebz apparently the former possibility takes place, but in $Cu(NCO)_2(2\text{-meiz})_2$ and β-$Cu(NCO)_2(2\text{-etbz})_2$ according to the I.R. implications, nitrogens rather than oxygens occupy the axial sites.

The spectrum of α-$Cu(NCO)_2(2\text{-etbz})_2$ indicates [19, 23] an expressively tetragonal structure, showing barely weak axial bonding with cyanate oxygens.

The complexes of 1-meiz and 2-etiz have their $d \leftarrow d$ bands lying at 14000 and 15100 $cm^{-1}$ respectively, accompanied by high wavenumber shoulders above 17000 $cm^{-1}$. Hathaway *et al.* [25] found similar electronic spectra for a series of mono(diethylenetriamine)copper(II) complexes, which was considered as consistent with a rhombic octahedral or square pyramidal stereochemistry. Very recently, Hathaway *et al.* [26] reported for regular trigonal bipyramidal $[Cu\{tris(2\text{-aminoethyl})amine\}(NH_3)]^{2+}$ cation an electronic spectrum showing also a high wavenumber shoulder, but as a whole shifted in respect of our cases by *ca.* 3000 $cm^{-1}$ to lower energies. From these facts it may be concluded that 1-meiz and 2-etiz complexes should have five-coordinate or rhombic octahedral stereochemistries;

TABLE IV. Magnetic Susceptibility Data for α- and β-$Cu(NCO)_2(2\text{-etbz})_2$.

| T (K) | 294 | 252.8 | 223.1 | 193.4 | 163.7 | 143.9 | 124.1 | 104.3 | 94.4 | |
|---|---|---|---|---|---|---|---|---|---|---|
| α-$Cu(NCO)_2(2\text{-etbz})_2$ | | | | | | | | | | |
| $10^6 \chi_M^{corr}$ (cgsu) | 1457 | 1685 | 1920 | 2186 | 2620 | 3005 | 3499 | 4020 | 4479 | C = 0.407 ± 0.008 cgsu |
| $\mu_{eff}$ (B.M.) | 1.82 | 1.82 | 1.825 | 1.82 | 1.83 | 1.84 | 1.85 | 1.82 | 1.83 | $\theta = -(3.77 \pm 3.74)$ K<br>$\mu_{eff}^{t.i.} = 1.81$ B.M.[a] |
| β-$Cu(NCO)_2(2\text{-etbz})_2$ | | | | | | | | | | |
| $10^6 \chi_M^{corr}$ (cgsu) | 1510 | 1720 | 1969 | 2263 | 2662 | 3008 | 3460 | 4157 | 4601 | C = 0.421 ± 0.007 cgsu |
| $\mu_{eff}$ (B.M.) | 1.845 | 1.83 | 1.84 | 1.845 | 1.845 | 1.84 | 1.84 | 1.85 | 1.85 | $\theta = -(1.07 \pm 2.95)$ K<br>$\mu_{eff}^{t.i.} = 1.84$ B.M.[a] |

[a] Calculated according to the relation $\mu_{eff}^{t.i.} = 2.83\ C^{1/2}$

a more distinct structural assignment is difficult to carry out at this stage. Recently it was pointed out [27] that the connection between the copper(II) atom stereochemistry and the solid state electronic spectrum is not always straightforward.

### *Magnetic Properties*

All the complexes under study have room temperature values of the magnetic moments in the range of 1.82–1.88 B.M. This is in keeping with magnetically diluted tetragonal Cu(II) systems showing an orbitally non-degenerate ground state [19b].

The temperature-variable magnetic data for both isomers of $Cu(NCO)_2(2\text{-etbz})_2$ are given in Table IV. The magnetic susceptibilities of these compounds obey the Curie–Weiss law, $\chi_M^{corr} - N_A\alpha = C(T + \theta)^{-1}$, where $N_A\alpha$ is the temperature independent paramagnetism; this was calculated as described previously [28]. The values of C and $\theta$ were determined by the standard linear least squares method (95% CI). The small $\theta$ values suggest that significant exchange interactions between the Cu(II) atoms do not take place in the pertinent temperature range. This is somewhat surprising for the β-isomer, where the presence of exchange coupling is indicated by the ESR spectrum (see above). Apparently the effectiveness of the spin transmission is insufficient to become evident by the temperature dependence of the magnetic susceptibility.

## Conclusions

According to the results of the physical methods the cyanato–copper(II) complexes of imidazole ligands have elongated octahedral stereochemistry, formed by *trans*-$Cu(NCO)_2L_2$ units. These units are stacked in the crystal structure in such a way that weaker axial bonds of the Cu(II) atoms with cyanate oxygens or nitrogens arise.

In the complexes of iz, 1,2-dimeiz, 2-mebz and in α-$Cu(NCO)_2(2\text{-etbz})_2$ axial Cu–O bonds may be assumed, but in $Cu(NCO)_2(2\text{-meiz})_2$ and β-$Cu(NCO)_2(2\text{-etbz})_2$ then Cu–N bonds are assumed. In the complexes of 1-meiz and 2-etiz, five coordinate geometries are possible. The two isomers of $Cu(NCO)_2(2\text{-etbz})_2$ differ by the degree of axial distortion as a consequence of the different bridging function of the NCO groups.

The stereochemical propositions deduced from the electronic spectra, together with the far-I.R. and ESR evidence, indicate a manifestation of an equatorial–axial interaction [29]. In the case of the studied complexes the strengthening of axial interactions is accompanied by a loosening of bonds in the equatorial plane, and *vice versa*.

## Acknowledgements

We are indebted to Dr. M. Nádvorník from the Department of General and Inorganic Chemistry, University of Chemical Technology, Pardubice for the temperature-variable susceptibility measurements. We are also grateful to Mrs. O. Lakatošová and M. Belovičová for technical assistance.

## References

1 Part XX: J. Kohout, J. Mroziński and M. Hvastijová, *Z. Naturforsch.*, *37b*, 102 (1982).

2 Abbreviations used: iz = imidazole, bz = benzimidazole, me = methyl, et = ethyl.

3 B. K. S. Lundberg, *Acta Chem. Scand.*, *26*, 3977 (1972).

4 W. J. Eilbeck, F. Holmes and A. E. Underhill, *J. Chem. Soc. A*, 757 (1967).

5 M. Goodgame and L. I. B. Haines, *J. Chem. Soc. A*, 174 (1966).

6 W. J. Eilbeck, F. Holmes, C. E. Taylor and A. E. Underhill, *J. Chem. Soc. A*, 128 (1968).

7 D. M. L. Goodgame, M. Goodgame and G. W. Rayner-Canham, *Inorg. Chim. Acta*, *3*, 399 (1969).

8 A. Mašlejová and J. Kohout, *Z. Anorg. Allg. Chem.*, accepted for publication.

9 M. A. Phillips, *J. Chem. Soc.*, 2393 (1928).

10 J. Kohout, M. Hvastijová, A. Mašlejová, J. Gažo and L. Omelka, *Z. Anorg. Allg. Chem.*, *434*, 29 (1977).

11 J. Kohout, M. Quastlerová-Hvastijová and J. Gažo, *Coll. Czech. Chem. Comm.*, *39*, 3417 (1974).

12 M. Quastlerová-Hvastijová, J. Kohout, J. Gažo and F. Valach, *J. Inorg. Nucl. Chem.*, *38*, 705 (1976).

13 (a) M. de N. D. Cordes and J. L. Walter, *Spectrochim. Acta*, *24A*, 237 (1968);
(b) M. de N. D. Cordes and J. L. Walter, *ibid.*, *24A*, 1421 (1968);
(c) C. Perchard and A. Novak, *ibid.*, *23A*, 1953 (1967);
(d) C. Perchard and A. Novak, *J. Chim. Phys.*, *65*, 1964 (1968).

14 J. Kohout, M. Hvastijová and J. Gažo, *Coord. Chem. Rev.*, *27*, 141 (1978).

15 (a) F. Valach, M. Dunaj-Jurčo and M. Handlovič, *J. Cryst. Mol. Struct.*, *10*, 61 (1980);
(b) F. Valach and M. Dunaj-Jurčo, *Acta Crystallogr.*, in press.

16 J. Kohout, M, Kabešová, M. Hvastijová and J. Gažo, *Coll. Czech. Chem. Comm.*, *43*, 379 (1978).

17 (a) J. B. Hodgson, C. C. Percy and D. A. Thornton, *J. Mol. Struct.*, *66*, 81 (1980);
(b) J. Reedijk, *Rec. Trav. Chim. Pays-Bas*, *88*, 1451 (1969).

18 J. Gažo, I. B. Bersuker, J. Garaj, M. Kabešová, J. Kohout, H. Langfelderová, M. Melník, M. Serátor and F. Valach, *Coord. Chem. Rev.*, *19*, 253 (1976).

19 (a) B. J. Hathaway and D. E. Billing, *Coord. Chem. Rev.*, *5*, 143 (1970);
(b) I. M. Procter, B. J. Hathaway and P. Nicholls, *J. Chem. Soc. A*, 1678 (1968).

20 J. Reedijk, J. C. A. Windhorst, N. H. M. Ham and W. L. Groeneveld, *Rec. Trav. Chim. Pays-Bas*, *111*, 234 (1971).

21 J. W. Searl, R. C. Smith and S. J. Wyard, *Proc. Phys. Soc.*, *78*, 1174 (1961).

22 D. W. Smith, *J. Chem. Soc. A*, 3108 (1970).

23 B. J. Hathaway, *J Chem. Soc.*, *Dalton Trans.*, 196 (1972).

24 G. Ivarson, *Acta Chem. Scand.*, *27*, 3523 (1973).

25 M. J. Bew, B. J. Hathaway and R. J. Fereday, *J. Chem. Soc.*, *Dalton Trans.*, 1229 (1972).

26 M. Duggan, N. Ray, B. Hathaway, G. Tomlinson, P. Brint and K. Pelin, *J. Chem. Soc.*, *Dalton Trans.*, 1342 (1980).

27 (a) A. Sedov, M. Dunaj-Jurčo, M. Kabešová, J. Gažo and J. Garaj, *Inorg. Chim. Acta Letts*, *64*, L257 (1982);
(b) A. Sedov, M. Kabešová, M. Dunaj-Jurčo, J. Gažo and J. Garaj, *Koord. Khim.*, in press.

28 F. Valach, J. Kohout, M. Dunaj-Jurčo, M. Hvastijová and J. Gažo, *J. Chem. Soc.*, *Dalton Trans.*, 1867 (1979).

29 J. Gažo, R. Boča, E. Jóna, M. Kabešová, L. Macášková, P. Pelikán, J. Šima and F. Valach, *Coord. Chem. Rev.*, in press.