NITROSODICYANOMETHANIDE COMPLEXES OF Cu(II) AND Co(II) WITH METHYLPYRAZOLES; NUCLEOPHILIC ADDITIONS AND COLIGAND ISOMERS

Maria HVASTIJOVA[a], Jiri KOHOUT[a], Darina KOVACOVA[a] and Renate SKIRL[b]

[a] *Department of Inorganic Chemistry,*
Slovak Technical University, 812 37 Bratislava, The Slovak Republic
[b] *Department of Chemistry,*
Martin Luther University, Halle-Wittenberg, 06120 Halle (Saale), Germany

From the M(II)–ONC(CN)$_2^-$–L systems, where M = Cu or Co and L = pyrazole (pz), 3(5)-methyl-pyrazole (mpz), 3,4,5-trimethylpyrazole (tmpz), or indazole (inz), the following new compounds were prepared: [M{ONC(CN)$_2$}$_2$L$_4$] with M = Cu, L = pz; M = Co, L = pz, mpz, inz; [M{ONC(CN)$_2$}$_2$L$_2$] with M = Cu, L = tmpz, inz; M = Co, L = tmpz; [M{L.ONC(CN)$_2$}$_2$] with M = Cu, L = mpz; M = Co, L = tmpz. All compounds were studied by thermal decomposition and by infrared and electronic spectroscopy, the Cu(II) complexes also by ESR spectroscopy. Six-coordinate octahedral or pseudooctahedral structures were assigned to complexes of all the types. Nitroso-dicyanomethanide is nitroso-*N*-bonded and in the [M{OCN(CN)$_2$}$_2$L$_2$] complexes is involved in the bidentate bridging. The [M{L.ONC(CN)$_2$}$_2$] complexes contain anionic chelate ligands formed by nucleophilic addition of the *N*(imine)−*C*(cyano) type in the M(II) coordination sphere. The first coligand isomer pair with Co(II) central atom is presented.

Previously we investigated the copper(II), nickel(II) and cobalt(II) complexes containing cyanate[1–5], dicyanamide[6–9] and tricyanomethanide groups[8–10] and ligands of the pyrazole type. In many of the systems studied, nucleophilic addition of the pyrazole imine nitrogen to the carbon of the pseudohalide CN group takes place giving rise to a new anionic chelate ligand. The normal pseudohalide complexes were also isolated from such systems, forming with the corresponding metal chelates coligand isomers[1–6,8,10,11].

We have been continuing in this research by using an additional nonlinear pseudo-halide, viz. the nitrosodicyanomethanide anion, ONC(CN)$_2^-$ (refs[12,13]). Since this anion contains, in addition to the cyano groups, also a nitroso group, it was of interest to examine how the anion is bonded in metal complexes, including the possibility of bridging. Its tendency to nucleophilic addition to pyrazole bases in the metal coordination sphere was investigated as well.

In this paper we studied compounds isolated from the M(II)–ONC(CN)$_2^-$–L systems, where M = Cu and Co and L = pyrazole (pz), 3,5-methylpyrazole (mpz), 3,4,5-trimethylpyrazole (tmpz), and indazole, i.e. benzopyrazole (inz).

EXPERIMENTAL

Preparation of the Compounds

A solution of 5.0 mmol of Cu(NO$_3$)$_2$. 3 H$_2$O or Co(NO$_3$)$_2$. 6 H$_2$O in 40 cm^3 of water and a solution of 11 mmol of pyrazole base in 4 cm^3 of methanol were added to a solution of 11.0 mmol of KONC(CN)$_2$ in 5 cm^3 of water. The compound precipitated from the stirred system in the form of a microcrystalline powder.

[Cu{ONC(CN)$_2$}$_2$(pz)$_4$], [Cu{mpz.ONC(CN)$_2$}$_2$] and [Cu{ONC(CN)$_2$}$_2$(inz)$_2$] emerged as oily substances which, after a short stirring, transformed into microcrystalline precipitates.

For the preparation of [Co{ONC(CN)$_2$}$_2$(tmpz)$_2$] the solutions of the reactants were refrigerated and the reaction was conducted while cooling the system constantly.

[Co{tmpz.ONC(CN)$_2$}$_2$] was obtained at room temperature or at 40 °C. From an oily substance obtained after stirring and 24 h of standing in a refrigerator, a microcrystalline product was separated.

The products were filtered off, washed with methanol and dried in a desiccator over KOH.

We attempted to obtain complexes of the [M{ONC(CN)$_2$}$_2$L$_2$] type, since only such complexes undergo nucleophilic addition between the coordinated pyrazole base and pseudohalide[14]. However, only the [M{ONC(CN)$_2$}$_2$L$_4$] type was frequently isolated from the M(II)–ONC(CN)$_2^-$–L systems containing the components in the 1 : 2 : 2 ratio.

Analyses

Metals were determined chelatometrically after decomposing the compounds with dilute H$_2$SO$_4$ and oxidizing the organic component with K$_2$S$_2$O$_8$. Elemental analysis was carried out by using a Carlo Erba C,H,N-analyzer. The analytical results and some other characteristic data are given in Table I.

Physico-Chemical Measurements

Infrared spectra (4 000 – 200 cm^{-1}) of the compounds in KBr disks and Nujol mulls were recorded using a Philips Analytical PU9800 FTIR spectrometer. Electronic and ESR spectra were obtained as in ref.[15] and ref.[16], respectively.

RESULTS AND DISCUSSION

Infrared Spectra

The bands characteristic of the ONC(CN)$_2$ and L.ONC(CN)$_2$ (L = mpz, tmpz) ligands and the bands due to the M–N stretching vibrations were assigned (Table II) by comparison with the spectra of free pyrazole and its derivatives[17–21] as well as of other complexes containing pyrazoles as ligands[1–5,19–21].

The expressive shift of the nitrosodicyanomethanide ν_{as}(NCO) and ν_s(NCO) vibrations to higher frequencies as compared with those of the free anion indicates that in all

the complexes studied the anion is bonded through the nitrogen of the nitroso group[12,13,22–25]. This is in agreement with the finding made by Kohler et al.[12,13,22–25] for the nitrosodicyanomethanide complexes of *d*-metals. Other nitrosodicyanomethanide frequencies, e.g. $\nu(C\equiv N)$, are changed only slightly and not very significantly.

However, the ligand field spectra (see next section) give evidence that the $[M\{OCN(CN)_2\}_2L_2]$ complexes are six-coordinate, and therefore all of the $ONC(CN)_2$ groups must be involved in the bidentate bridging through their cyano nitrogens. This is the only way the six-coordinate complexes can be formed, because neither the chemi-

TABLE I
Analytical data and other basic properties of the complexes

Compound	Colour	Decomposition temperature[a] °C	Calculated/Found			
			% C	% H	% N	% M
$[Cu\{ONC(CN)_2\}_2(pz)_4]$	dark green	127	41.26	3.08	37.43	12.27
			40.60	2.98	37.03	12.13
$[Cu\{mpz.ONC(CN)_2\}_2]$	dark green	130	40.44	2.91	33.68	15.28
			40.30	2.88	33.17	15.11
$[Cu\{ONC(CN)_2\}_2(tmpz)_2]$	green	140	45.81	4.27	29.68	13.46
			45.03	4.22	28.81	13.18
$[Cu\{ONC(CN)_2\}_2(inz)_2]$	green	120	49.23	2.91	28.71	13.02
			48.44	3.04	28.41	13.09
$[Co\{ONC(CN)_2\}_2(pz)_4]$	orange	137	41.63	3.11	37.76	11.35
			40.85	3.01	37.47	11.40
$[Co\{ONC(CN)_2\}_2(mpz)_4]$	brick red	145	45.92	4.20	34.08	10.24
			45.52	4.16	33.47	10.08
$[Co\{ONC(CN)_2\}_2(tmpz)_2]$	orange	180	46.26	4.31	29.97	12.61
			45.97	4.44	29.31	12.44
$[Co\{tmpz.ONC(CN)_2\}_2]$	beige brown	120	46.26	4.31	29.97	12.61
			46.03	4.25	29.55	12.49
$[Co\{ONC(CN)_2\}_2(inz)_4]$	yellow orange	170	56.75	3.36	27.25	8.19
			55.97	3.44	26.83	8.27

[a] Determined with 100 mg of samples using a heating rate of 6 °C/min.

TABLE II
Important vibrational frequencies of the complexes in the 4 000 – 200 cm^{-1} region

Compound	ν(C≡N)	ν(C=N)	ν_{as}(CNO)	ν_{s}(CNO)	ν(C–C) ν(C–N)[a]	ν(M–N)
KONC(CN)$_2$ (ref.[24])	2 232 – 2 225		1 325	1 275	1 236	
[Cu{ONC(CN)$_2$}$_2$(pz)$_4$]	2 219 vs, 2 213 sh		1 398 w	1 348 s	1 210 vs, 1 187 sh	279 m, 253 m
[Cu{mpz.ONC(CN)$_2$}$_2$]	2 220 vs	1 625 s	1 398 s	1 335 s	1 250 w, 1 233 sh[b] 1 208 sh, 1 190 vs	322 ms, 304 m, 292 m
[Cu{ONC(CN)$_2$}$_2$(tmpz)$_2$]	2 221 vs		1 398 s	1 352 mw	1 191 vs	317 s, 270 m
[Cu{ONC(CN)$_2$}$_2$(inz)$_2$]	2 233 s, 2 207 s		1 392 s	1 353 s	1 233 mw[b]	309 sh, 300 mw, 280 m
[Co{ONC(CN)$_2$}$_2$(pz)$_4$]	2 221 vs		1 390 s	1 370 m	1 209 vs, 1 205 vs 1 197 vs	309 mw, 286 m, 246 s
[Co{ONC(CN)$_2$}$_2$(mpz)$_4$]	2 227 s, 2 215 m		1 385 vs	1 366 vs	1 213 vs, 1 203 sh	306 m, 246 m
[Co{ONC(CN)$_2$}$_2$(tmpz)$_2$]	2 238 vs, 2 219 vs		1 390 vs	[c]	1 233 s[d], 1 205 s[d] 1 191 s	312 m, 272 w, 249 s
[Co{tmpz.ONC(CN)$_2$}$_2$]	2 238 vs, 2 220 vs	1 632 vs	1 407 s	1 340 s	1 227 s, 1 211 s[d] 1 207 sh[d]	308 mw, 267 ms[b], 241 ms
[Co{ONC(CN)$_2$}$_2$(inz)$_4$]	2 229 ms, 2 215 s		1 405 m	1 350 ms[b]	1 184 vs	300 sh, 293 sh, 285 ms, 259 m

[a] This vibration appears in the complexes with chelate ligands; [b] cannot be distinguished with certainty from the ligand band; [c] not assigned owing to the interference with ligand bands; [d] one from these absorptions can be due to the ligand vibration.

cal analysis nor the infrared patterns indicate the presence of any additional ligand such as water or methanol from the reaction system.

Köhler and Seifert[12,13] demonstrated that in the case of an additional cyano nitrogen bonding of nitrosodicyanomethanide, another $\nu(C\equiv N)$ band can be observed at about 2 260 cm^{-1}. Although for some of the compounds studied by us the $\nu(C\equiv N)$ frequency is split, this splitting occurs for complexes of the two stoichiometries to a similar extent and therefore this phenomenon is not associated with the nitrosodicyanomethanide bridges.

In the spectra of {Cu{mpz.ONC(CN)$_2$}$_2$] and [Co{tmpz.ONC(CN)$_2$}$_2$], the bands of the ONC(CN)$_2$ vibrations are present but new strong bands also appear in the 1 650 cm^{-1} range. These bands can be attributed to the $\nu(C=N)$ vibrations as in the case of the [Cu{pz.C(CN)$_3$}$_2$] and [M{L.N(CN)$_2$}$_2$] complexes, where M = Cu or Ni and L is a pyrazole base[3,6,8,10,26]. Hence, it is reasonable to assume that in the coordination sphere of the Cu(II) or Co(II) central atom, nucleophilic addition involves bonding of the pyrazole imine nitrogen to the carbon of one of the cyano groups and simultaneous transfer of the imine hydrogen (Scheme 1).

The electron drift towards the nitrogen atom of the coordinated nitroso group would bring about considerable electron dilution at the carbon atom of the cyano group. So this atom becomes strongly electrophilic and is adapted for a nucleophilic attack from the pyrazole imine nitrogen with a rather acidic hydrogen, migrating to the cyano nitrogen. This assumption is based on the results of the molecular orbital study[27] of the nucleophilic addition leading to the [Cu(3,5-dimethylpyrazole.NCO)$_2$] system. For the latter complex the nucleophilic addition was evidenced by X-ray crystallographic analysis[28]; in the present case, however, preparation of suitable crystals failed.

The assignment of the $\nu(C-N)$ bands is less certain because strong bands of the $\nu(C-C)$ vibration are also present in the 1 200 cm^{-1} range. It should be noted that with Co(II) no pure compound with anionic chelate ligand formed by nucleophilic addition of the type pyrazole base-pseudohalide was isolated till now.
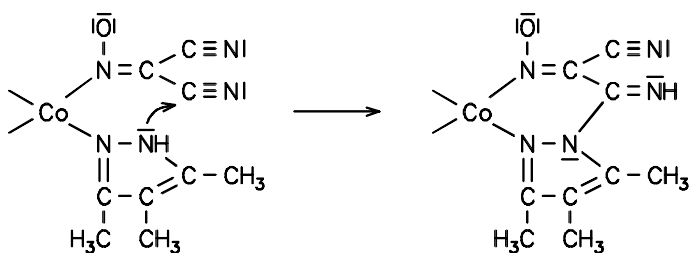
SCHEME 1

Far-Infrared Spectra

In the far-infrared region (down to 200 cm^{-1}) there occur two to four absorptions which can be attributed to the M−N stretching vibrations. Although some mixing of the vibrations which involve different nitrogen atoms must be expected, some relations are quite evident. For [Cu{ONC(CN)$_2$}$_2$(pz)$_4$], two bands occur fairly below 300 cm^{-1} which very probably belong to the stretching associated with the Cu−N(pz) bonds in the equatorial plane[1,19–21]. Thus, species of the effective D_{2h} symmetry are formed, completed by two long axial copper bonds through the nitrogen atoms of the nitroso group; the corresponding stretching vibrations should have very low frequencies (much below 200 cm^{-1}).

All the other nitrosodicyanomethanide complexes exhibit, in addition to the M−N(L) bands whose position approaches that for the Cu(II)–pz complex, bands in the 300 cm^{-1} range, which may be due to the stretching vibrations of the short metal bonds with the nitroso nitrogens of the ONC(CN)$_2$ groups. The frequencies reveal a strengthening of the M−NO bonds compared with the M−NC bonds in the tricyanomethanide complexes of the pyrazole and pyridine ligands[8,10,15,16].

In the [Cu{ONC(CN)$_2$}$_2$L$_2$] complexes the ONC(CN)$_2^-$ anions are in the bridging function and form through their CN groups long axial links to the neighbouring Cu(II) atoms. For the Co(II)–tmpz complex the situation is similar but the length of the axial bonds approaches closely that of the in-plane bonds; the band at 272 cm^{-1} may be associated with the Co−NC stretching. From the ν(Cu−N) values for [Cu{ONC(CN)$_2$}$_2$L$_2$] it can be inferred that weakening of the Cu–NO bonds is accompanied by a strengthening of the Cu−N(L) bonds, similarly to the case of the [Cu(NCO)$_2$L$_2$] and [Cu(NCS)$_2$L$_2$] complexes where L is the methylpyridine ligand[29].

The ν(Cu−N) frequencies for Cu{mpz.ONC(CN)$_2$}$_2$ indicate some strengthening of the equatorial Cu−N bonding system whereas, surprisingly, in Co{tmpz.ONC(CN)$_2$}$_2$ the Cu−N bonds appear to be weaker than in its nitrosodicyanomethanide isomer. This fact is also manifested by a lower thermal stability of the Co(II) chelate.

Electronic Spectra

The electronic spectral data including ligand field and intra-ligand absorptions are given in Table III.

All nitrosodicyanomethanide complexes of Cu(II) exhibit broad *d–d* bands tailing appreciably into the near-infrared region, occasionally with ill-resolved shoulders. This is in agreement with the distorted octahedral environment of nitrogen donors around the Cu(II) atom[30,31]. The positions of the bands which probably involve the ^2E_g, $^2B_{2g} \leftarrow {}^2B_{1g}$ tetragonal transitions (some rhombic splitting is possible), are nearly constant. As it seems, the influence of basicity and steric effects of the neutral ligands on their ligand field strength are mutually well-balanced. The low energy shoulders assigned to the $^2A_{1g} \leftarrow {}^2B_{1g}$

transition in D_{4h} indicate that the tetragonal distortion increases from the tmpz to the inz complex.

The compound [Cu{mpz.ONC(CN)$_2$}$_2$] shows a similar type of d–d spectrum as the foregoing compounds and hence, possesses an analogous pseudooctahedral configuration. However, the shift of the d–d band maximum to higher energies suggests a stronger ligand field effect of the chelating donors and probably a stronger axial distortion, as has been found in many analogous cases[1,3,4,6,8].

The ligand field spectra of the nitrosodicyanomethanide Co(II) complexes, both 1 : 4 and 1 : 2, indicate octahedral structures[32,33] and the low and high energy absorption bands are attributed to the $^4T_{2g} \leftarrow {}^4T_{1g}$ (F) and $^4T_{1g}$ (P) $\leftarrow {}^4T_{1g}$ (F) transitions, respectively. The changes in the 10 Dq values are relatively small, only for the mpz system a perceptible reduction appears. The β values, lying within narrow limits about 0.8, reveal a medium degree of covalency[34].

TABLE III
Electronic and ESR spectral data for the complexes

Compound	$\tilde{v}_{max}$, μm^{-1}	$g_{\parallel}$	$g_{\perp}$	$\bar{g}^a$	G^b
KONC(CN)$_2$ (ref.[24])	≈1.89 sh, br^b, 2.37, 2.94				
[Cu{ONC(CN)$_2$}$_2$(pz)$_4$]	1.65, ≈2.16 sh, 2.41			2.077^c	
[Cu{mpz.ONC(CN)$_2$}$_2$]	1.71	2.165	2.052	2.090	3.17
[Cu{ONC(CN)$_2$}$_2$(tmpz)$_2$]	≈1.33 sh, 1.65, 2.74	2.166	2.062	2.097	2.68
[Cu{ONC(CN)$_2$}$_2$(inz)$_2$]	≈1.40 sh, 1.63, ≈2.50 sh, br^b	^{d}	2.055		

		10 Dq, μm^{-1}	B, μm^{-1}		β
[Co{ONC(CN)$_2$}$_2$(pz)$_4$]	0.99, ≈2.04 sh, br^b, ≈2.52 sh	1.11	0.0780		0.80
[Co{ONC(CN)$_2$}$_2$(mpz)$_4$]	0.95, 2.03^e, ≈2.49 sh, 2.69 sh	1.05	0.0783		0.81
[Co{ONC(CN)$_2$}$_2$(tmpz)$_2$]	0.98, 2.00^e, ≈2.50 sh	1.10	0.0759		0.78
[Co{tmpz.ONC(CN)$_2$}$_2$]	≈0.78 sh, br^b, 0.93, ≈1.53 sh, ≈1.65 sh, ≈1.83 sh, ≈1.89 sh, ≈2.13 sh, ≈2.50 sh, br^b				
[Co{ONC(CN)$_2$}$_2$(inz)$_4$]	0.98, ≈2.07 sh, br^b, ≈2.58 sh	1.10	0.0808		0.83

^{a} Calculated from the relation $\bar{g} = [(g_{\parallel}^2 + 2g_{\perp}^2)/3]^{1/2}$; ^{b} calculated from the relation $G = (g_{\parallel} - 2)/(g_{\perp} - 2)$; ^{c} g value in the inflexion point of the quasi-isotropic signal; ^{d} not resolved; ^{e} wavenumber in the centre of gravity of the broad absorption.

The d–d spectrum of $[Co\{tmpz.ONC(CN)_2\}_2]$ has a low-wavenumber shoulder on the near-infrared band, and also its absorption band in the visible region shows a multiple structure on the low-wavenumber side. This spectral feature gives evidence of a tetragonally distorted octahedral stereochemistry, where each octahedral orbital triplet is split into an orbital doublet and a singlet[32,35,36]. The two absorption bands with the lowest energy can be attributed to the transitions from the ground state ($^4E_g^a$ or $^4A_{2g}^a$) to the $^4B_{2g}$ and $^4E_g^b$ excited states; the assignment of higher energy absorption bands is uncertain. The completion of the square-planar chelate species (see Scheme 1) to the tetragonal bipyramide occurs through the CN groups of the adjacent chelate units resulting in axial bonding.

In the high-energy region (ca 2.0 – 3.0 μm^{-1}) one or two absorption bands are present belonging to the transitions in the coordinated $ONC(CN)_2^-$ anion[23]; they are easily discernible from the d–d absorptions which lie within the same spectral range.

ESR Spectra

The ESR data of the copper(II) complexes in the polycrystalline state at ambient temperature are given in Table III. The Cu(II)–pz complex shows a quasi-isotropic, broad (ΔB_{pp} = 17 mT) signal, from which only the average g-value can be determined. The remaining spectra are of the axial type but they are broad, especially in the $g_{\rm II}$ region, so that this g factor component could not always be evaluated. Unresolved hyperfine splitting and, particularly, exchange coupling between magnetically non-equivalent Cu(II) atoms in the unit cell are responsible for these ESR features[10,30,31,37,38]. In some cases, the exchange coupling is also manifested by low values of the G parameter[30,31,38]. However, the lower g-values between ca 2.05 – 2.06 are consistent with the $d_{x^2-y^2}$ ground state[30,31]. In polymeric $[Cu\{ONC(CN)_2\}_2(tmpz)_2]$ and $[Cu\{mpz.ONC(CN)_2\}_2]$, exchange coupling can propagate through the bridge links but in molecular $[Cu\{ONC(CN)_2\}_2(pz)_4]$ the exchange coupling patterns are apparently more complex.

CONCLUSIONS

It was verified that with respect to d-metals, nitrosodicyanomethanide behaves as a nitroso-nitrogen bonded ligand. This anion can also be involved in bidentate bridging, most probably through its cyano group. However, its bridging ability is less pronounced than that of tricyanomethanide or dicyanamide or cyanate. This can be documented by the formation of the 1 : 4 complexes with monodentate nitrosodicyanomethanide being preferred to that of the bridged 1 : 2 complexes. The bridging ability of the pseudo-halides under consideration decreases roughly in the following order:

$$C(CN)_3^- \approx N(CN)_2^- > NCO^- > ONC(CN)_2^- \quad .$$
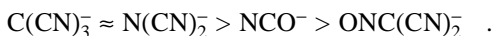
The first case of nucleophilic addition and the first coligand isomer pair with Co(II) central atom have been discovered.

REFERENCES

1. Hvastijova M., Kohout J., Gazo J.: J. Inorg. Nucl. Chem. *43*, 2337 (1981).
2. Hvastijova M., Kohout J., Gazo J.: J. Coord. Chem. *12*, 27 (1982).
3. Kohout J., Hvastijova M.: Inorg. Chim. Acta *131*, 33 (1987).
4. Hvastijova M., Kohout J., Gazo J.: Polyhedron *3*, 1147 (1984).
5. Hvastijova M., Kohout J., Adamikova A., Fodran P.: J. Coord. Chem. *14*, 259 (1986).
6. Mrozinski J., Kohout J., Hvastijova M., Kohler H.: Transition Met. Chem. (Weinheim, Germany) *11*, 481 (1986).
7. Hvastijova M., Kohout J., Okruhlica M., Mrozinski J., Jager L.: Transition Met. Chem. (Weinheim, Germany) *18*, 579 (1993).
8. Hvastijova M., Kohout J., Kohler H., Ondrejovic G.: Z. Anorg. Allg. Chem. *566*, 111 (1988).
9. Mrozinski J., Kohout J., Hvastijova M.: Polyhedron *8*, 157 (1989).
10. Kozisek J., Hvastijova M., Kohout J., Mrozinski J., Kohler H.: J. Chem. Soc., Dalton Trans. *1991*, 1773.
11. Kohout J., Mrozinski J., Hvastijova M.: Polyhedron *4*, 1975 (1985).
12. Kohler H., Eichler B., Salewski R.: Z. Anorg. Allg. Chem. *379*, 183 (1970).
13. Skopenko V. V., Zub Yu. L., Bolelii V. F., Kohler H.: Koord. Khim. *10*, 1317 (1984).
14. Hvastijova M., Kohout J., Kohler H., Gazo J.: *Proc. 10th Conf. Coord. Chem., Smolenice-Bratislava 1985*, p. 161. Bratislava 1985.
15. Hvastijova M., Kohout J., Wusterhausen H., Kohler H.: Z. Anorg. Allg. Chem. *510*, 37 (1984).
16. Kohout J., Hvastijova M., Kohler H., Omelka L.: Collect. Czech. Chem. Commun. *55*, 435 (1990).
17. Zecchina A., Cerutti L., Coluccia S., Borello E.: J. Chem. Soc., B *1967*, 1363.
18. Hvastijova M., Kohout J.: Unpublished results.
19. Reedijk J.: Rec. Trav. Chim. Pays-Bas *88*, 1451 (1969).
20. Reedijk J.: Rec. Trav. Chim. Pays-Bas *90*, 117 (1971).
21. Reedijk J., van Ooijen J. A. C.: J. Chem. Soc., Dalton Trans. *1978*, 1170.
22. Kohler H., Seifert B.: Z. Anorg. Allg. Chem. *360*, 137 (1968).
23. Kohler H., Seifert B.: Z. Anorg. Allg. Chem. *379*, 1 (1970).
24. Kohler H., Bolelii V. F., Skopenko V. V.: Z. Anorg. Allg. Chem. *468*, 179 (1980).
25. Fritsch E., Polborn K., Sunkel K., Kohler H., Jager L., Beck W.: Z. Anorg. Allg. Chem. *617*, 110 (1992).
26. Hvastijova M., Kohout J., Klimcikova J., Kohler H.: J. Coord. Chem. *15*, 409 (1987).
27. Boca R., Hvastijova M., Kohout J.: J. Coord. Chem. *33*, 137 (1994).
28. Valach F., Kohout J., Dunaj-Jurco M., Hvastijova M., Gazo J.: J. Chem. Soc., Dalton Trans. *1979*, 1867.
29. Kohout J., Kabesova M., Hvastijova M., Gazo J.: Collect. Czech. Chem. Commun. *43*, 379 (1978).
30. Hathaway B. J., Billing D. E.: Coord. Chem. Rev. *5*, 143 (1970).
31. Hathaway B. J.: J. Chem. Soc., Dalton Trans. *1972*, 1196.
32. Lever A. B. P.: *Inorganic Electronic Spectroscopy*, p. 480. Elsevier, Amsterdam 1984.
33. Cotton F. A., Wilkinson G.: *Advanced Inorganic Chemistry*, p. 729. Wiley, New York 1988.
34. Jorgensen C. K.: *Absorption Spectra and Chemical Bonding in Complexes*, p. 134. Pergamon Press, Oxford 1962.

35. Lever A. B. P.: Coord. Chem. Rev. *43*, 63 (1982).
36. Lever A. B. P., Walker I. M., McCarthy P. J.: Inorg. Chim. Acta *14*, 177 (1975).
37. Lancaster J. C., McWhinnie W. R., Welham P. L.: J. Chem. Soc., A *1971*, 1742.
38. Bew M. J., Hathaway B. J., Fereday R. J.: J. Chem. Soc., Dalton Trans. *1972*, 1229.

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