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Copper(II) and Nickel(II) Alkylxanthate Complexes (R = C_2H_5, *i*-C_3H_7, *i*-C_4H_9, *s*-C_4H_9, and C_5H_{11}): EPR and Solid-State ^{13}C CP/MAS NMR Studies

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Abstract—Alkylxanthate complexes of the general formula $[M\{S(S)COR\}_2]$ (M = Ni, ^{63}Cu, and ^{65}Cu; R = C_2H_5, *i*-C_3H_7, *i*-C_4H_9, *s*-C_4H_9, and C_5H_{11}) were synthesized and studied by EPR and high-resolution solid-state ^{13}C CP/MAS NMR. In the copper(II) complexes stabilized in the matrix of nickel(II) compounds, square planar chromophores $[CuS_4]$ are characterized by rhombic distortion (EPR data). Experimental EPR spectra were simulated at the second order of perturbation theory. Nickel(II) complexes were characterized by ^{13}C NMR spectra. In all cases, the –OC(S)S– groups were found to exhibit intramolecular structural equivalence.

Xanthate derivatives have found a wide practical application as additives to lubricating oils, antioxidants for polyolefins, etc. However, alkylxanthates are mainly used in flotation concentration of nonferrous metal sulfide ores. Hence, it is of interest to investigate complexation between transition metals and alkylxanthate ligands for better understanding of how the flotation reagent ions interact with the surface of mineral species.

Previously [1], the structures of VO^{2+} complexes with alkylxanthates and their chemical properties in reactions of the adduct formation with cyclic S-donor bases were studied by EPR. The structures of copper(II) alkylxanthate complexes were investigated in the matrices of corresponding thallium(I) complexes [2]. Analysis of resolved super-hyperfine structure (HFS) from thallium atoms in the experimental EPR spectra made it possible to identify heteropolynuclear Cu(II)-Tl(I) complexes of the general formula $[CuTl_6(Xan)_8]$ (Xan = $ROC(S)S^-$; R = C_2H_5, C_3H_7, and C_4H_9) in the magnetically diluted systems studied. These heptanuclear complexes are generated from paramagnetic copper(II) compounds and diamagnetic matrices of thallium(I) complexes and exhibit the Jahn–Teller dynamic effect.

In this study, EPR and high-resolution solid-state ^{13}C CP/MAS NMR techniques were used to investigate the structures and spectroscopic properties of the complexes $[M\{S(S)COR\}_2]$ (M = Ni(II) and Cu(II)) containing alkylxanthate ligands $ROC(S)S^-$ (R = C_2H_5, *i*-C_3H_7, *i*-C_4H_9, *s*-C_4H_9, and C_5H_{11}).

EXPERIMENTAL

Ni(II) complexes of the formula $[Ni\{S(S)COR\}_2]$ (R = C_2H_5 (**I**), *i*-C_3H_7 (**II**), *i*-C_4H_9 (**III**), *s*-C_4H_9 (**IV**), and C_5H_{11} (**V**)) were synthesized by reactions of Ni^{+2} with the corresponding alkylxanthate ions in aqueous solutions. Voluminous greenish yellow precipitates were washed by decantation, filtered off, and dried in air. Individual copper(II) alkylxanthate complexes cannot be isolated because they are immediately involved in the intermolecular redox reaction yielding copper(I) compounds and the corresponding dixanthogens:

$$2Cu^{2+} + 4ROC(S)S^- = 2[Cu(S_2COR)_2]$$
$$= [Cu_2(S_2COR)_2] + ROC(S)S\text{–}S(S)COR.$$

Copper(II) complexes of the formula $[Cu\{S(S)COR\}_2]$ (R = C_2H_5 (**VI**), *i*-C_3H_7 (**VII**), *i*-C_4H_9 (**VIII**), and C_5H_{11} (**IX**)) were synthesized in a state magnetically diluted with the corresponding Ni(II) compounds (Cu : Ni = 1 : 1000). Such a technique allows one to stabilize $[Cu\{S(S)COR\}_2]$ molecules in the matrix of nickel(II) complexes (except for plastic $[Ni\{S(S)CO\text{-}s\text{-}C_4H_9\}_2]$) and study their structures and spectroscopic properties. Copper(II) complexes were obtained as isotope-substituted compounds from isotope-enriched copper salts containing ^{63}Cu (99.3(1) at. %) and ^{65}Cu (99.2(1) at. %).

Sodium and potassium alkylxanthates (Cheminova Agro A/S and Hoechst) were additionally characterized by ^{13}C MAS NMR data:

$Na\{S_2COC_2H_5\}$ (δ, ppm): 231.1, 230.0, 229.5 ($–S_2CO–$), 73.4, 72.6 ($–OCH_2–$), 15.9, 14.5, 14.1 ($–CH_3$).

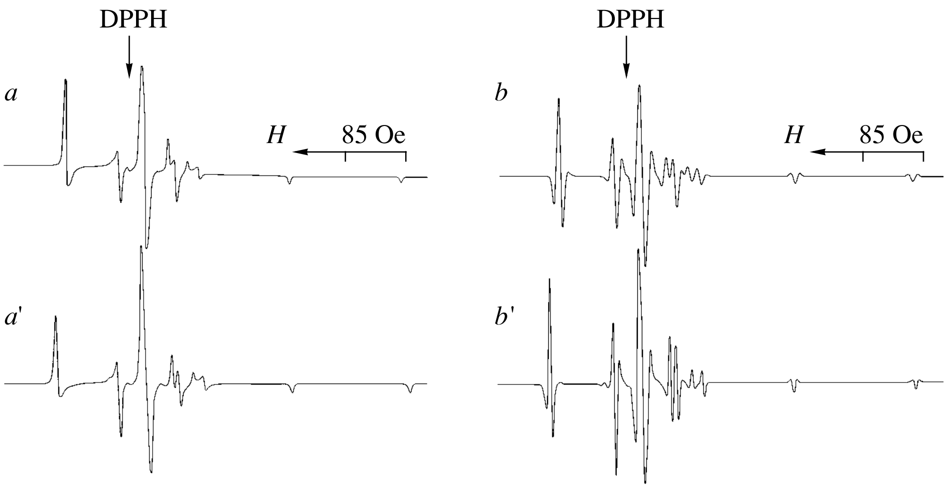

Fig. 1. Experimental EPR spectra of magnetically Ni(II)-diluted isotope-substituted complexes of the formula $[^{63/65}Cu\{S(S)COC_2H_5\}_2]$ as the (*a*, *a*') first and (*b*, *b*') third derivatives for (*a*, *b*) ^{63}Cu and (*a*', *b*') ^{65}Cu isotopes.

$Na\{S_2CO\text{-}i\text{-}C_3H_7\}$ (δ, ppm): 231.8 ($-S_2CO-$), 79.2 (–OCH=), 23.5, 20.6 (1 : 1, $-CH_3$).

$Na\{S_2CO\text{-}i\text{-}C_4H_9\}$ (δ, ppm): 233.4, 232.8, 232.4, 229.9 ($-S_2CO-$), 81.2 ($-OCH_2-$), 28.5 (–CH=), 21.7, 21.1, 20.2 ($-CH_3$).

$Na\{S_2CO\text{-}s\text{-}C_4H_9\}$ (δ, ppm): 231.9 ($-S_2CO-$), 84.0, 83.7 (–OCH=), 30.0, 29.2 ($-CH_2-$), 19.4, 17.2 (1 : 1, $-CH_3$), 12.0 ($-CH_3$).

$K\{S_2COC_5H_{11}\}$ (δ, ppm): 234.0, 233.5 ($-S_2CO-$), 80.9, 75.5 (1 : 3, $-OCH_2-$), 35.0, 28.5, 27.5, 23.2, 20.8, 17.9 ($-CH_2-$), 17.0, 14.5, 12.5 ($-CH_3$).

EPR spectra were recorded on a 70-02 XD/1 radiospectrometer (~9.5 GHz, MP SZ, Minsk) at ~295 K. The working frequency was measured with a ChZ-46 microwave frequency meter. *g* Factors were calculated with reference to DPPH. The errors in *g* value and HFS constant (Oe) determination were ±0.002 and ±2%, respectively. The EPR parameters were refined by simulating the experimental spectra within the second order of perturbation theory with the use of the WIN-EPR SimFonia program (Bruker Co. software, version 1.2).

The simulation was performed in two steps. First, theoretical EPR spectra were simulated for first derivatives and finally approximated for second and third derivatives characterized by substantially narrower resonance signals. In the approximation, *g* values, HFS constants, resonance line widths, and contributions (in percent) from the Lorentz and Gauss components to the line shape were varied.

Room-temperature ^{13}C NMR spectra were recorded on a CMX-360 pulse spectrometer (90.52 MHz; Chemagnetics Infinity Co., USA) with a superconducting magnet ($B_0 = 8.46$ T) and a Fourier transform. The $^{13}C-{}^1H$ cross polarization technique was used. The $^{13}C-{}^1H$ dipolar couplings were suppressed via proton decoupling in a magnetic field with the corresponding proton resonance frequency [3]. Samples (~350 mg) of the complexes were placed in a zirconium dioxide rotor 7.5 mm in diameter. The spinning rates in ^{13}C MAS NMR experiments were 2700 to 5500 Hz; the number of scans was 256 to 2820; the duration of proton $\pi/2$ pulses was 4.5 μs; the $^1H-{}^{13}C$ contact time was 2.0 to 5.0 ms; excitation pulses were spaced at 2.0 s.

Isotropic ^{13}C chemical shifts δ (ppm) are referenced to a line of crystalline adamantane used as the external standard (δ 38.56 ppm relative to tetramethylsilane [4]). The width of a reference line for crystalline adamantane (2.1 Hz) was used to check the homogeneity of the magnetic field. The isotropic chemical shifts were corrected for drift of the magnetic field strength during the NMR experiments (its frequency equivalent for ^{13}C nuclei was 0.051 Hz/h). Chemical shifts and integrated intensity ratios for overlapping signals in the ^{13}C NMR spectra were additionally refined by fragment-by-fragment simulation considering line positions and widths and contributions from the Lorentz and Gauss components to the line shapes.

RESULTS AND DISCUSSION

Experimental EPR spectra of magnetically diluted copper(II) alkylxanthate complexes (Figs. 1, 2) are nearly axially symmetric, which suggests the square planar structure of chromophores $[CuS_4]$ with predominant localization of the unpaired electron at the Cu $3d_{x^2-y^2}$ AO. Therefore, the complexes obtained contain the sp^2d-hybridized copper atom (s- + p_x- + p_y- + $d_{x^2-y^2}$ AO) and, since the 4*d* AO is involved, can be classified as outer-orbital ones (in contrast to the corresponding inner-orbital nickel(II) compounds).

In all cases, the computer simulation of the experimental spectra revealed noticeable anisotropy of *g* and

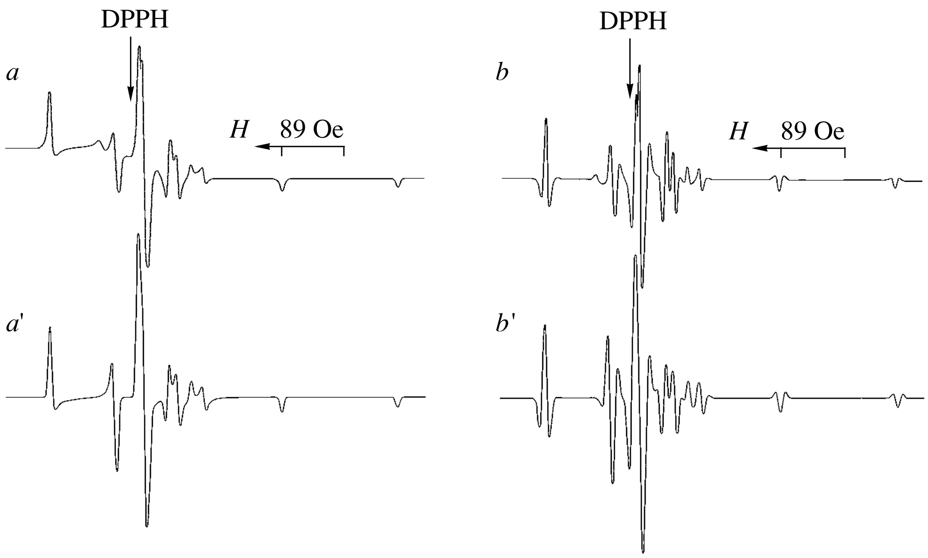

Fig. 2. (*a*, *b*) Experimental and (*a*', *b*') simulated EPR spectra of magnetically Ni(II)-diluted isotope-substituted bis(O-isobutylxanthato)copper(II), $[^{65}Cu\{S(S)CO\text{-}i\text{-}C_4H_9\}_2]$, as the (*a*, *a*') first and (*b*, *b*') third derivatives.

A tensors in the *xy* plane (Figs. 1, 2; Table 1), which can be attributed to rhombic distortion of the chelate unit $[CuS_4]$ due to diagonal nonequivalence of the Cu–S bonds. These conclusions are fully consistent with X-ray diffraction data for the molecular structures of some nickel(II) alkylxanthate complexes [5–18] and their adducts with N-donor bases [19]. One can state that the EPR spectra of copper(II) complexes accurately reflect the structural features of nickel(II) alkylxanthates.

The experimental EPR parameters were refined by computer simulation. The best fit results are given in Table 1. The totality of the parameters unambiguously

Table 1. EPR parameters of magnetically diluted copper(II) alkylxanthate complexes

Complex	g_1	A_1(Cu)*	g_2	A_2(Cu)*	g_3	A_3(Cu)*
$[Cu(S_2COC_2H_5)_2]$	2.094	156/167	2.029	35/38	2.022	32/34
$[Cu(S_2CO\text{-}i\text{-}C_3H_7)_2]$	2.085	154/165	2.026	39/42	2.021	35/37
$[Cu(S_2CO\text{-}i\text{-}C_4H_9)_2]$	2.084	155/166	2.026	39/42	2.019	35/37
$[Cu(S_2COC_5H_{11})_2]$	2.086	152/163	2.028	42/45	2.023	34/36

* The HFS constants are given for $^{63}Cu/^{65}Cu$ nuclei.

Table 2. Chemical shifts (δ, ppm; Me_4Si) of the signals in the ^{13}C NMR spectra of crystalline nickel(II) complexes of the formula $[Ni\{S(S)COR\}_2]$

Complex	–OC(S)S–	$–OCH_2–$	–OCH=	–CH=	$–CH_2–$	$–CH_3$
$[Ni(S_2COC_2H_5)_2]$	230.9	71.5				14.2
$[Ni(S_2CO\text{-}i\text{-}C_3H_7)_2]$	229.9		81.4			23.9, 23.0 (1 : 1)
$[Ni(S_2CO\text{-}i\text{-}C_4H_9)_2]$	231.8	81.8		29.0		21.6, 19.8 (1 : 1)
$[Ni(S_2CO\text{-}s\text{-}C_4H_9)_2]$	230.6		85.6, 84.7		30.6	21.1
Melt	230.4		83.3 d (148.5)*		30.0 t (126.7)*	13.2, 11.9 20.7 q (127.6)* 10.9 q (126.1)*
$[Ni(S_2COC_5H_{11})_2]$	231.2	80.1, 75.8 (1 : 3)			35.6, 28.5 (1 : 3) 27.7, 26.5 (3 : 1) 22.8	16.9, 14.5, 12.0 (1 : 2 : 1)

* The spin–spin coupling constants $^1J(^{13}C–^1H)$, Hz (d, t, and q denote doublet, triplet, and quadruplet, respectively).

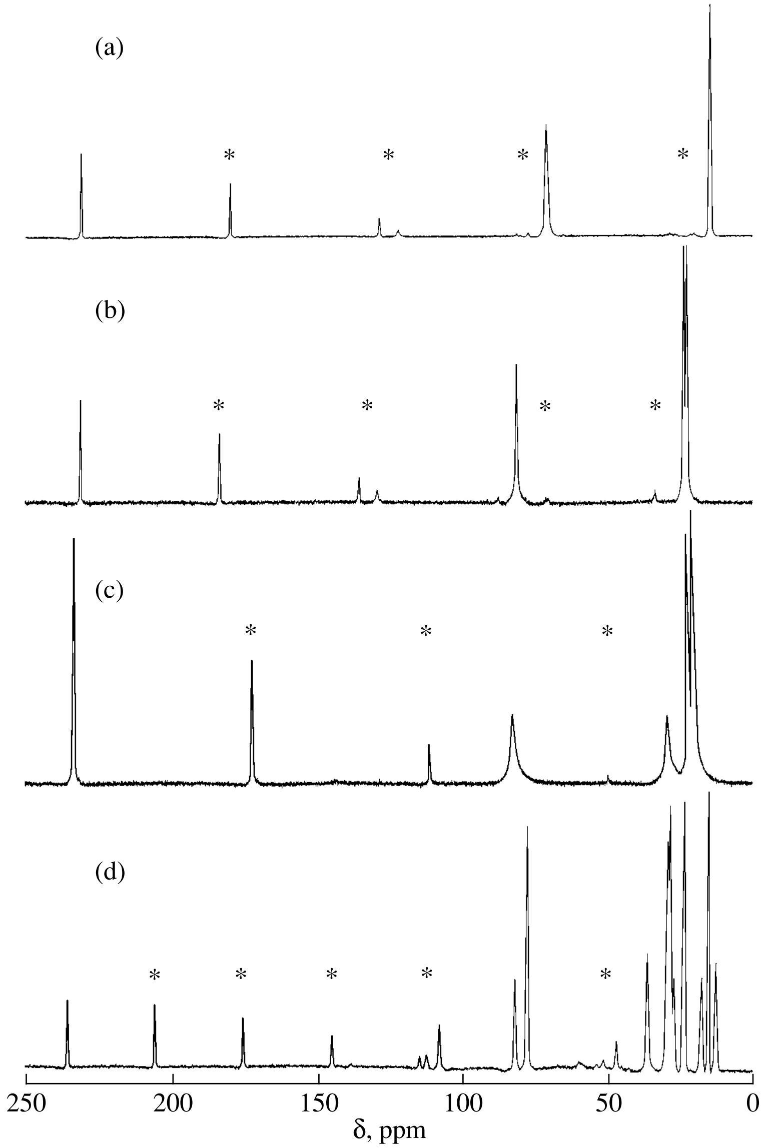

Fig. 3. ^{13}C NMR spectra of polycrystalline complexes [Ni{S(S)COR}$_2$] at 295 K (R = (a) C_2H_5, (b) *i*-C_3H_7, (c) *i*-C_4H_9, and (d) C_5H_{11}); number of scans/spinning rate are 1000/4600, 256/4300, 2820/5500, and 600/2700 Hz, respectively. Components obtained as a result of incomplete averaging of the anisotropy of the ^{13}C chemical shift in the MAS experiment are asterisked.

indicates the S-homogeneous environment of the copper atom in all the complexes obtained. The EPR spectra contain characteristic quartets of the resolved HFS from the $^{63/65}$Cu nucleus (I = 3/2) in all the three orientations and an additional intense high-field peak of "extra feature" [20, 21]. Comparative analysis revealed a high qualitative similarity of the simulated and experimental EPR spectra. The former fit very exactly to the latter as regards the positions and relative intensities of not only the HFS components of all the three orientations but also the additional peak, which is not at all represented parametrically in the simulation.

According to the ^{13}C NMR data, all the nickel(II) complexes obtained are individual compounds (Fig. 3, Table 2). The spectra contain resonance signals due to –OC(S)S– fragments and the alkyl groups at the O atom. The –OC(S)S– fragments are manifested by a single signal in the ^{13}C NMR spectra (Fig. 3, Table 2), which suggests the structural equivalence of the xanthate ligands in complexes **I**–**V**. This correlates with the mononuclear centrosymmetric structure of nickel(II) alkylxanthates [5–18].

Interestingly, in many nickel(II) dialkyldithiocarbamate complexes, which are structurally close to alkyl-xanthate ones, the –C(S)S– fragments exhibit both intra- and intermolecular nonequivalence [22]. According to the ^{13}C NMR data, the δ values of the –OC(S)S– fragments are systematically much higher (230 to 232 ppm)

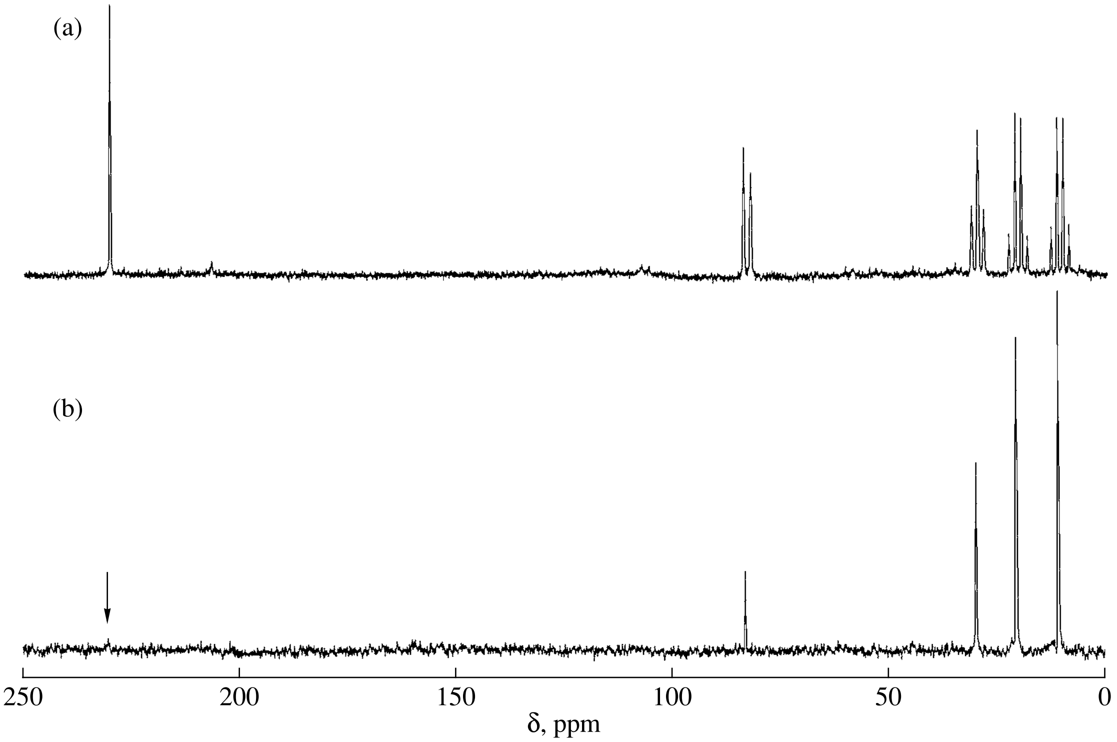

Fig. 4. ^{13}C NMR spectra of melted $[Ni\{S(S)CO\text{-}s\text{-}C_4H_9\}_2]$ at 295 K (a) without and (b) with proton decoupling (numbers of scans are 152 and 300, respectively). The signal of the –OC(S)S– fragment is marked with an arrow.

than those of the =NC(S)S– groups in nickel(II) dialkyldithiocarbamate complexes (203–209 ppm), which is due to the stronger displacement of the electron density from the C atom of the –C(S)S– fragments in alkylxanthate complexes.

In the MAS experiments for $[Ni(S_2CO\text{-}s\text{-}C_4H_9)_2]$, the sample partially melted near the rotor walls (where the centrifugal forces are maximum). The ^{13}C NMR spectrum of this phase of complex **IV** (Fig. 4a), which was recorded with a one-90°-pulse sequence, shows ^1H–^{13}C couplings (Table 2). Proton decoupling makes the ^{13}C NMR spectrum significantly simpler (Fig. 4b). The change in the state of aggregation systematically lowers the ^{13}C chemical shifts of the corresponding groups in melted complex **IV** compared to its solid state.

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REFERENCES

1. Ivanov, A.V., Baratova, Z.R., and Solozhenkin, P.M., *Zh. Neorg. Khim.*, 1994, vol. 39, no. 6, p. 992.
2. Ivanov, A.V., Solozhenkin, P.M., Ovchinnikov, I.V., and Shvengler, Ph.A., *Koord. Khim.*, 1987, vol. 13, no. 7, p. 892.
3. Pines, A., Gibby, M.G., and Waugh, J.S., *J. Chem. Phys.*, 1972, vol. 56, no. 4, p. 1776.
4. Earl, W.L. and VanderHart, D.L., *J. Magn. Reson.*, 1982, vol. 48, no. 1, p. 35.
5. Chen, H.W. and Fackler, J.P., *Inorg. Chem.*, 1978, vol. 17, no. 1, p. 22.
6. Hoskins, B.F., Tiekink, E.R.T., and Winter, G., *Inorg. Chim. Acta*, 1985, vol. 105, no. 2, p. 171.
7. Hoskins, B.F., Tiekink, E.R.T., and Winter, G., *Z. Kristallogr.*, 1985, vol. 172, no. 4, p. 257.
8. Edwards, A.J., Hoskins, B.F., and Winter, G., *Aust. J. Chem.*, 1986, vol. 39, no. 11, p. 1983.
9. Prisyazhnyuk, A.I., Bel'skii, V.K., and Kolchinskii, E.V., *Koord. Khim.*, 1987, vol. 13, no. 7, p. 977.
10. Romanenko, G.V., Podberezskaya, N.V., and Bakakin, V.V., *Zh. Strukt. Khim.*, 1987, vol. 28, no. 1, p. 98.
11. Abrahams, B.F., Hoskins, B.F., Tiekink, E.R.T., *et al.*, *Aust. J. Chem.*, 1988, vol. 41, no. 7, p. 1117.
12. Tiekink, E.R.T. and Winter, G., *Rev. Inorg. Chem.*, 1992, vol. 12, p. 183.
13. Cox, M.J. and Tiekink, E.R.T., *Z. Kristallogr.*, 1996, vol. 211, no. 2, p. 111.

14. Cox, M.J. and Tiekink, E.R.T., *Z. Kristallogr.*, 1996, vol. 211, no. 6, p. 350.
15. Cox, M.J. and Tiekink, E.R.T., *Z. Kristallogr.*, 1996, vol. 211, no. 8, p. 575.
16. Cox, M.J. and Tiekink, E.R.T., *Z. Kristallogr.*, 1996, vol. 211, no. 11, p. 750.
17. Xiong, R.-G., Liu, C.-M., Li, H.-Zh., *et al.*, *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.*, 1996, vol. 52, no. 3, p. 519.
18. Cox, M.J. and Tiekink, E.R.T., *Z. Kristallogr.*, 1999, vol. 214, no. 4, p. 242.
19. Pang, L., Lucken, E.A.C., and Bernardinelli, G., *J. Am. Chem. Soc.*, 1990, vol. 112, no. 24, p. 8754.
20. Ovchinnikov, I.V. and Konstantinov, V.N., *J. Magn. Reson.*, 1978, vol. 32, no. 2, p. 179.
21. Rieger, Ph.H., *Electron Spin Resonance (Senior Reporter Symons M.C.R.)*, vol. 13B, Newcastle Upon Tyne: Athenaeum, 1993, p. 178.
22. Ivanov, A.V., Ivakhnenko, E.V., Forsling, W., *et al.*, *Zh. Neorg. Khim.*, 2002, vol. 47, no. 3, p. 468.