Effect of Adduct Formation and Self-association on Electron Spin Resonance Spectra and Electronic Structure of Copper(II) Diethyldithiocarbamate and Di-isopropyl Dithiophosphate †

By **Nicola D. Yordanov** * and **Dimitar Shopov**, Institute of Organic Chemistry, Bulgarian Academy of Sciences, 1113 Sofia, Bulgaria

The solid-state e.s.r. spectra of copper(II) diethyldithiocarbamate and di-isopropyl dithiophosphate dissolved in co-ordinating and non-co-ordinating solvents are compared with single-crystal and powdered samples diluted with the corresponding complexes of Ni^{II} and Zn^{II}. The e.s.r. spectra of $[Cu(S_2CNEt_2)_2]$ and $[Cu\{S_2P(OPr^i)_2\}_2]$ dissolved in non-co-ordinating solvents are similar to those obtained from solid samples where weak self-association is present. E.s.r. spectra of copper(II) adducts are similar to those obtained from self-associated copper(II) complexes in the solid state. On the basis of the present results, it is suggested that in the ground state the unpaired electron is in a hybrid orbital of the $d_{x^2-y^2}$, d_{z^2}, and 4*s* atomic orbitals of copper. The coefficients of this molecular orbital show that the effects of adduct formation or self-association increase the contribution of the d_{z^2} and 4*s* orbitals to the ground state.

ELECTRON SPIN RESONANCE studies have shown that copper(II) complexes are more ionic after adduct formation with Lewis bases;[1-5] the molecular-orbital coefficients calculated from the e.s.r. parameters [1,2,5] have shown however that the equatorial metal–ligand σ bonds are more covalent. Similar results were observed [6,7] for copper(II) complexes which were magnetically diluted with the corresponding diamagnetic complexes of various metal ions, both in the powder and single-crystal state. In the solid state the complexes are usually affected by self-association. Both effects, adduct formation and self-association, are very similar in character and in the present paper we compare their influence on the shape and parameters of the e.s.r. spectra, and on the electronic structure of the copper complexes respectively. Both effects are a result of the interaction along the *z* axis of the complexes between the donor atoms of one or two molecules and the metal ion from another molecule.

The available *X*-ray data show that the distances between the metal ion and the axial atoms are usually larger than the distances between the metal ion and the equatorial atoms; the metal ion–axial ligand atom distances are shorter for larger metal ion–equatorial atom distances. The *X*-ray data also show that when self-association is present the equatorial distances are not equal in the *x* and *y* directions. This finding confirms the e.s.r. data which suggest that the adduct formation and self-association change the electronic structure of the complexes to a more ionic structure.

We report here our studies on copper(II) dithiocarbamate, $[Cu(S_2CNEt_2)_2]$, and dithiophosphate, $[Cu\{S_2P(OPr^i)_2\}_2]$, complexes which were magnetically diluted with the corresponding nickel(II) and zinc(II) complexes in the solid state; results are also reported

---

† Presented at the Autumn Meeting of the Chemical Society, Leicester, September 1974.

[1] N. D. Yordanov and D. Shopov, *Inorg. Chim. Acta*, 1971, **5**, 679.

[2] O. M. Petruchin, I. N. Marov, V. V. Jukov, Yu. N. Dubrov, and A. N. Ermakov, *Russ. J. Inorg. Chem.*, 1972, **17**, 1876.

[3] H. A. Kuska, M. T. Rogers, and R. E. Drullinger, *J. Phys. Chem.*, 1967, **71**, 109.

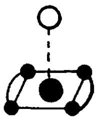
[4] H. R. Gersman and J. D. Swalen, *J. Chem. Phys.*, 1962, **36**, 3221.

[5] N. D. Yordanov and D. Shopov, *Proc. 13th Internat. Conf. Co-ordination Chem.*, Poland, 1970, vol. 1, p. 121.

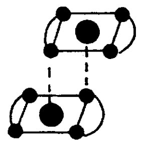
[6] M. J. Weeks and J. P. Fackler, *Inorg. Chem.*, 1968, **7**, 2548.

[7] G. Rist, J. Ammeter, and H. H. Gunthard, *J. Chem. Phys.*, 1968, **49**, 2210.

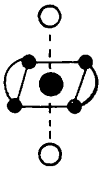
on the interaction of these complexes with some Lewis bases, added in solution.



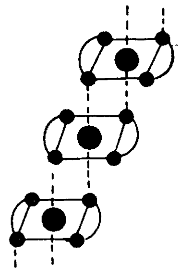
1 : 1 Adduct



Two molecules self-associated



1:2 Adduct



Three molecules self-associated

EXPERIMENTAL

Copper(II), nickel(II), and zinc(II) diethyldithiocarbamates and di-isopropyl dithiophosphates, and mixtures of the copper and nickel and copper and zinc complexes, were prepared by a method described elsewhere.[8-10] The Cu : Ni and Cu : Zn ratios were *ca.* 1 : 100. All solvents used were purified and dried by standard methods.

E.s.r. spectra were recorded on a 3BS-X spectrometer, at 100 kHz magnetic-field modulation. All the other experimental conditions were as described elsewhere.[8-10]

RESULTS AND DISCUSSION

Typical e.s.r. spectra for $[Cu(S_2CNEt_2)_2]$ and $[Cu\{S_2P(OPr^i)_2\}_2]$ complexes recorded at room temperature are shown in Figure 1; the complexes were dissolved in non-co-ordinating (*a* and *b*) and in basic solvents (*c* and *d*). It may be seen from Figure 1 that adduct formation causes the magnitude of the g values to increase, and the hyperfine splitting constants to decrease. The lines are broadened due to fast exchange and the superhyperfine splitting (s.h.f.s.) from the two ^{31}P nuclei is observed only on the copper hyperfine (h.f.) line which corresponds to $m_I = -\frac{3}{2}$ [Figure 1 (*d*)]. The value of the s.h.f.s. is also decreased as a result of adduct formation.

Figure 2 shows the typical e.s.r. spectra for $[Cu(S_2CNEt_2)_2]$ dissolved in non-co-ordinating and in basic solvents in the solid state (77 K), and for powdered samples diluted with the corresponding nickel(II) and zinc(II) complexes. The shape and the parameters of the e.s.r. spectra in Figure 2 (*a*) and (*b*), as well as those in (*c*) and (*d*), are very similar. The spectra show the effect of adduct formation between $[Cu(S_2CNEt_2)_2]$ and Lewis bases in solution and that of self-association in the solid state. The sulphur atoms around the metal ion in $[Zn(S_2CNEt_2)_2]$ are considered to form a distorted square pyramid *via* a pseudo-dimeric structure.[11] The interaction in this dimer between the two copper ions through the sulphur atom is probably very strong since the total spin on magnetically condensed $[Cu(S_2CNEt_2)_2]$–$[Zn(S_2CNEt_2)_2]$ is $S = 1$.[12] The sample of $[Cu(S_2CNEt_2)_2]$ diluted by $[Zn(S_2CNEt_2)_2]$ did not show an e.s.r. spectrum in the half-field region of the magnetic field, indicating that there is no direct Cu–S–Cu interaction. On the other hand, $[Ni(S_2CNEt_2)_2]$ shows a rigorous four-co-ordinate structure.[13] We assume that the spectra in Figure 2 (*c*) and (*d*) are due to axial co-ordination of donor solvent molecules.

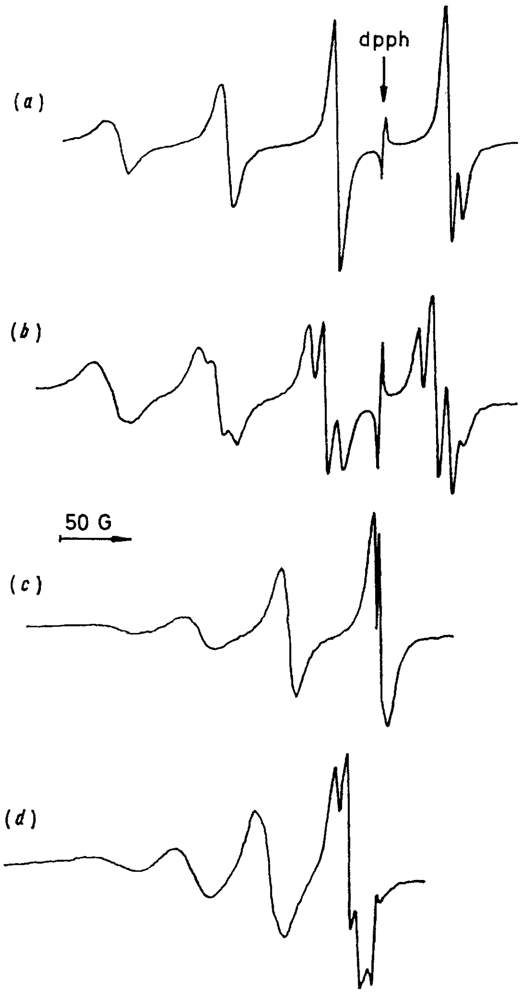


FIGURE 1 E.s.r. spectra of $[Cu(S_2CNEt_2)_2]$ and $[Cu\{S_2P(OPr^i)_2\}_2]$ complexes dissolved in toluene, hexane, and chloroform (*a* and *b*), and in pyridine (*c* and *d*) at 300 K

Analogous effects were also observed for $[Cu\{S_2$-

---

[8] D. Shopov and N. D. Yordanov, *Inorg. Chem.*, 1970, **9**, 1943.

[9] N. D. Yordanov and D. Shopov, *Compt. rend. Acad. bulg. Sci.*, 1970, **23**, 1239.

[10] N. D. Yordanov and D. Shopov, *Chem. Phys. Letters*, 1972, **16**, 60.

[11] M. Bonamico, G. Mazzone, A. Vaciago, and L. Zambonelli, *Acta Cryst.*, 1965, **19**, 898.

[12] J. F. Villa and W. E. Hatfield, *Inorg. Chim. Acta*, 1971, **5**, 145.

[13] M. Bonamico, G. Dessy, C. Mariani, A. Vaciago, and L. Zambonelli, *Acta Cryst.*, 1965, **19**, 619.

TABLE 1

E.s.r. parameters of copper(II) diethyldithiocarbamate and di-isopropyl dithiophosphate

Complex	Sample	$g_1 \pm$ 0.002	$g_2 \pm$ 0.002	$g_3 \pm$ 0.003	$\lvert A_1\rvert \pm$ 1G	$\lvert A_2\rvert \pm$ 1G	$\lvert A_3\rvert \pm$ 3G	$g_{\mathrm{iso.}}$	$\lvert A_{\mathrm{iso.}}\rvert$ G	$\lvert A_{\mathrm{a}}\rvert$ [a] G	$A(^{31}P)$	Ref.
$[Cu(S_2CNEt_2)_2]$–$[Ni(S_2CNEt_2)_2]$	Single crystal	2.020	2.025	2.084	36	42	159	2.043 [b]	79 [c]	40		6
	Powder		2.025	2.085		41	161	2.045 [b]	79 [c]	41		*d*
$[Cu(S_2CNEt_2)_2]$	Toluene		2.025	2.086		41	160	2.046	79	40		1, 9, *d*
$[Cu(S_2CNEt_2)_2]$–$[Zn(S_2CNEt_2)_2]$	Single crystal	2.025	2.033	2.107	7	27	143	2.055 [b]	59 [c]	42		6
	Powder		2.033	2.109		24	145	2.058 [b]	64 [c]	41		*d*
$[Cu(S_2CNEt_2)_2]$	90% toluene + 10% pyridine		2.033	2.111		24	145	2.059	64	41		9, *d*
$[Cu\{S_2P(OPr^i)_2\}_2]$–$[Ni\{S_2P(OPr^i)_2\}_2]$	Single crystal	2.018	2.023	2.079	30	36	159	2.040 [b]	75 [c]	42	9.3	10
	Powder		2.023	2.079		35	159	2.040 [b]	76 [c]	41	9.3	10, *d*
$[Cu\{S_2P(OPr^i)_2\}_2]$	Toluene		2.023	2.079		41	164	2.043	75		9.5	8,9, *d*
	90% toluene + 10% pyridine		2.032	2.111		20	140	2.058	60	40	8.7	1, *d*

[a] Obtained from the equation $A_{zz} = A_{\mathrm{iso.}} + 2A_{\mathrm{a}}$. [b] $g_{\mathrm{iso.}} = (g_1 + g_2 + g_3)/3$, or $(g_{\parallel} + 2g_{\perp})/3$. [c] $A_{\mathrm{iso.}} = (A_1 + A_2 + A_3)/3$ or $(A_{\parallel} + 2A_{\perp})/3$. [d] This work.

$P(OPr^i)_2\}_2]$. Figure 3 shows e.s.r. spectra of $[Cu\{S_2P(OPr^i)_2\}_2]$ dissolved in non-co-ordinating and in basic solvents at 77 K, and of powdered sample diluted with $[Ni\{S_2P(OPr^i)_2\}_2]$. If the s.h.f.s. from the two ^{31}P nuclei is neglected, the shape of these spectra is very similar to that of the spectra given in Figure 2.

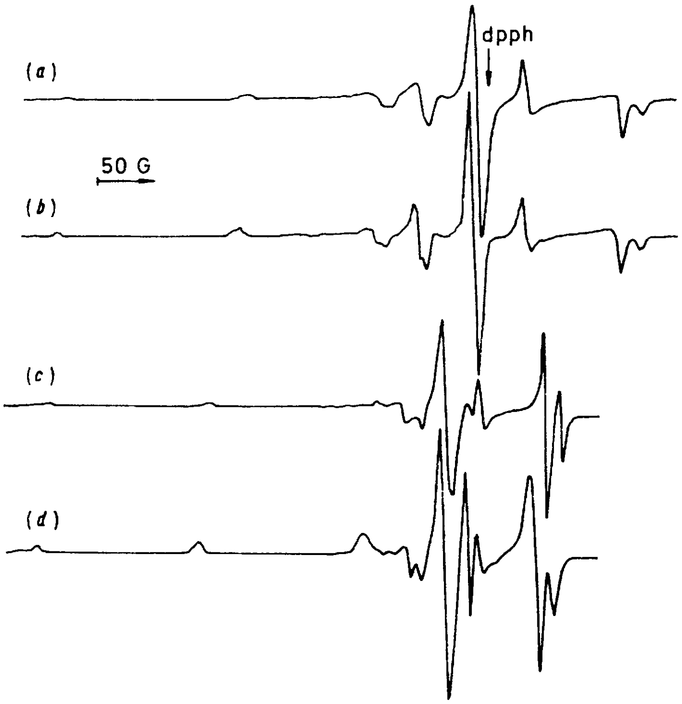


FIGURE 2 E.s.r. spectra of: (*a*), $[Cu(S_2CNEt_2)_2]$ dissolved in toluene at 77 K; (*b*) powdered sample of $[Cu(S_2CNEt_2)_2]$–$[Ni(S_2CNEt_2)_2]$ at 300 K; (*c*), powdered sample of $[Cu(S_2CNEt_2)_2]$–$[Zn(S_2CNEt_2)_2]$ at 300 K; (*d*), $[Cu(S_2CNEt_2)_2]$ dissolved in 90% toluene and 10% pyridine at 77 K

The data given in Table 1 show that $[Cu(S_2CNEt_2)_2]$ and $[Cu\{S_2P(OPr^i)_2\}_2]$ complexes dissolved in non-co-ordinating solvents, and magnetically diluted by the corresponding nickel(II) chelates, deviate slightly from axial symmetry. The complex $[Cu(S_2CNEt_2)_2]$ magnetically diluted by $[Zn(S_2CNEt_2)_2]$ shows a strong deviation from axial symmetry. For adducts and for self-associated complexes, the isotropic constants of the hyperfine interaction are decreased by 20—25% with respect to the same complexes, dissolved in non-co-ordinating solvents, or in a host lattice with a very weak interaction between the neighbouring molecules; $A_{\mathrm{aniso.}}$ is approximately constant in both cases. The results show that the contribution of the 4*s* orbital to the ground state of the unpaired electron is increased for adducts and self-associated complexes.

All these results show that the copper(II) complexes have approximately D_{4h} symmetry with a weak D_{2h}

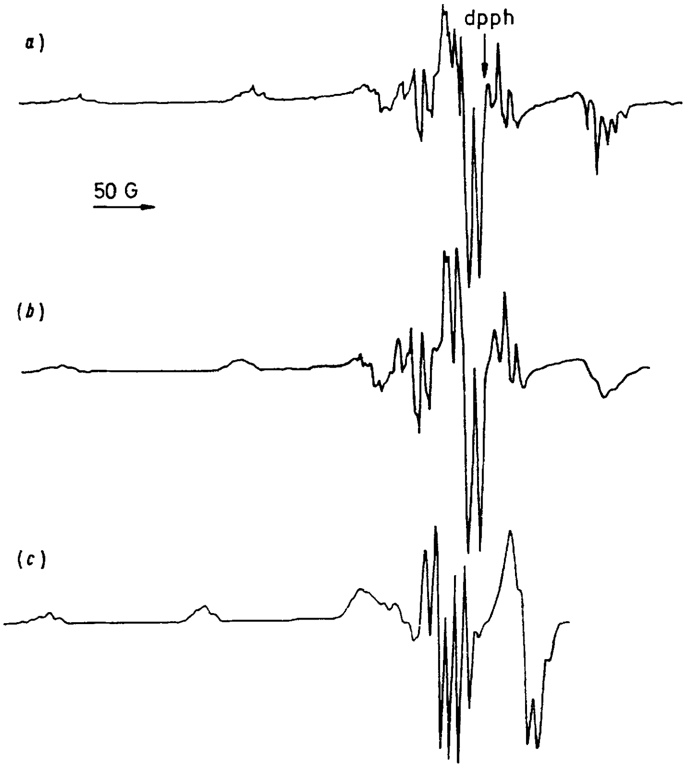


FIGURE 3 E.s.r. spectra of: (*a*) powdered sample of $[Cu\{S_2P(OPr^i)_2\}_2]$–$[Ni\{S_2P(OPr^i)_2\}_2]$ at 300 K; (*b*) $[Cu\{S_2P(OPr^i)_2\}_2]$ dissolved in toluene at 77 K; (*c*) $[Cu\{S_2P(OPr^i)_2\}_2]$ dissolved in 90% toluene and 10% pyridine at 77 K

perturbation. Thus we assume that in the ground state the unpaired electron is in the orbital described by the linear combination (1). Since the rhombic distortion

$$\psi = a|x^2 - y^2\rangle - b|3r^2 - z^2\rangle - c|4s\rangle \qquad (1)$$

of the crystal field is relatively weak, we assume that $a^2 \gg b^2, c^2$. Molecular orbital (2) can then be written.

$$\psi = \alpha(a|x^2 - y^2\rangle + b|3r^2 - z^2\rangle + c|4s\rangle) - \alpha'\psi_L \quad (2)$$

The coefficients in (2) were calculated from equations (3)—(9). Equations (3)—(5) are a slight modification of McGarvey's equations.[14]

$$a_{zz} = -P\left[\frac{4}{7}a^2\alpha^2 - \frac{1}{42}\left(14 - 3\cdot\frac{3a - 3^{\frac{1}{2}}b}{a + 3^{\frac{1}{2}}b}\right)\Delta g_{xx} - \right. \\ \left. - \frac{1}{42}\left(14 - 3\cdot\frac{3a + 3^{\frac{1}{2}}b}{a - 3^{\frac{1}{2}}b}\right)\Delta g_{yy} + \frac{2}{3}\Delta g_{zz}\right] \quad (3)$$

$$a_{xx} = -P\left[-\frac{2}{7}a^2\alpha^2 - \frac{4}{7}\,3^{\frac{1}{2}}ab + \frac{2}{3}\Delta g_{xx} - \right. \\ \left. \frac{1}{42}\left(14 + 3\cdot\frac{3a + 3^{\frac{1}{2}}b}{a - 3^{\frac{1}{2}}b}\right)\Delta g_{yy} - \frac{1}{21}\left(7 - \frac{3b}{a}\right)\Delta g_{zz}\right] \quad (4)$$

$$a_{yy} = -P\left[-\frac{2}{7}a^2\alpha^2 + \frac{4}{7}\,3^{\frac{1}{2}}ab - \frac{1}{42}\right. \\ \left.\left(14 + 3\cdot\frac{3a - 3^{\frac{1}{2}}b}{a + 3^{\frac{1}{2}}b}\right)\Delta g_{xx} + \frac{2}{3}\Delta g_{yy} - \frac{1}{21}\left(7 - \frac{3b}{a}\right)\Delta g_{zz}\right] \quad (5)$$

$$a_{ii} = A_{ii} - A_{iso.} \quad (6)$$

$$A_{iso.} = P(-K\alpha^2 + \Delta g) + A_{4s}c^2\alpha^2 \quad (7)$$

$$\Delta g = (\Delta g_{xx} + \Delta g_{yy} + \Delta g_{zz})/3 \quad (8)$$

$$\Delta g_{ii} = g_{ii} - 2.0023 \quad (9)$$

The choice of the values of the parameters will now be discussed. The magnitude of the isotropic h.f. interaction from the metal ion nucleus is due to the following factors: configuration interaction (K term); direct admixture of the 4*s* orbital to the ground state (A_{4s} term); and coupling of both the metal nuclear spin and the spin of the unpaired electron to the orbital motion of the electron (Δg term). The second and third terms have opposite signs to the first term, and they will be in competition with it; $A_{iso.}$ is usually negative for copper(II) complexes.[15] The K value is 0.42 for Cu^{II}, and it is assumed that it arises only from the configuration interaction, *i.e.* when D_{4h} symmetry is present and direct mixing of the 4*s* orbital with the ground state is precluded.* $P = g_e\beta_e\beta_N\langle d_{x^2-y^2}|r^{-3}|d_{x^2-y^2}\rangle = 360 \times 10^{-4}$ cm^{-1} (386 G), and has been estimated from unrestricted Hartree–Fock calculations;[16] $\lambda = -828$ cm^{-1} is the spin–orbit coupling constant for the free ion (in the gas phase).[17] The value of A_{4s} in equation (7) has been estimated as 980×10^{-4} cm^{-1} (1 046 G).[16] We assign the principal values of the g and A tensors (Table 1) as follows: $1 - x$, $2 - y$, and $3 - z$.

The calculated molecular-orbital coefficients are listed in Table 2. It may be seen that the contribution of the d_{z^2} and 4*s* orbitals to the ground state of the unpaired electron is small when the copper(II) complexes are dissolved in non-co-ordinating solvents, or the self-association is extremely weak. When rhombic distortion of the copper(II) complexes is present, as in the case of adducts and self-associated complexes, the contribution of the d_{z^2} and 4*s* orbitals is much larger. We assume that the coefficients listed in Table 2 are more adequate for the description of the real electronic structure of the complexes studied in this paper. Another argument supporting these results is the ^{31}P s.h.f.s. observed for [Cu{S$_2$P(OPr^i)$_2$}$_2$], arising from electron delocalization *via* sulphur atoms. The data on the s.h.f.s. constant (Table 1) show that in the case of adducts with [Cu{S$_2$P(OPr^i)$_2$}$_2$], α^2 increases when $a(^{31}P)$ is decreased.

TABLE 2

Molecular-orbital coefficients of copper(II) diethyldithiocarbamate and di-isopropyl dithiophosphate

Sample	α^2	a	b	c
$[Cu(S_2CNEt_2)_2]$–$[Ni(S_2CNEt_2)_2]$	0.6	0.845	0.0064	0.06
$[Cu(S_2CNEt_2)_2]$–$[Zn(S_2CNEt_2)_2]$	0.7	0.829	0.0336	0.21
$[Cu\{S_2P(OPr^i)_2\}_2]$–$[Ni\{S_2P(OPr^i)_2\}_2]$	0.6	0.855	0.0121	0.11

In some cases the adduct formation is followed by opening of the copper(II) chelate ring and co-ordination of one or two molecules of the base occurs in the *xy* plane of the complex.[18,19] On the basis of the above results we propose the following mechanism for these processes. The interaction between a copper(II) complex and a Lewis base along the *z* axis promotes the unpaired electron into a more hybridized molecular orbital, and increases the distortion in the *xy* plane. The metal–ligand bond length in the *xy* plane thus increases, and the co-ordination of a base in the *xy* plane of the copper(II) complex becomes more probable.

[5/250 *Received*, 6*th February*, 1975]

---

* The variation found by some authors in the magnitude of K is probably due to neglect of the contribution of the A_{4s} term in the calculation.

[14] B. R. McGarvey in 'Transition Metal Chemistry,' ed. R. L. Carlin, Marcel Dekker, New York, 1966, vol. 3, p. 89.

[15] B. R. McGarvey, *J. Phys. Chem.*, 1967, **71**, 51.

[16] A. J. Freeman and R. E. Watson, *Phys. Rev.*, 1961, **123**, 2027.

[17] D. Polder, *Physica*, 1942, **9**, 709.

[18] B. B. Wayland and M. D. Wisniewski, *Chem. Comm.*, 1971, 1025.

[19] N. D. Yordanov and D. Shopov, *Inorg. Nuclear Chem. Letters*, 1973, **9**, 19.