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Cyanato–Copper(II) Complexes with Organic Ligands. IX.[1] ESR Spectra and Magnetic Susceptibilities of Cyanato–Copper(II) Complexes with Ligands of the Aniline Group*

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The ESR spectra of complexes of formula $Cu(NCO)_2L_2$ where L = aniline, p-chloroaniline, p-bromoaniline, p-iodoaniline, o-, m-, and p-toluidine were recorded and their magnetic susceptibilities were measured at different temperatures. $Cu(NCO)_2(an)_2$ shows a normal orthorhombic, while $Cu(NCO)_2$ (o-tol)$_2$ exhibits a normal axial ESR spectrum (for abbreviations see note 2). Complexes with L = p-chloroan, p-bromoan, m-, and p-tol give "reversed" orthorhombic spectra and $Cu(NCO)_2$(p-iodoan)$_2$ displays a "reversed" axial spectrum; these results are interpreted as due to the presence of exchange interaction. The susceptibilities of all these complexes obey the Curie–Weiss law $\chi_M^{corr}\ \alpha(T+\Theta)^{-1}$ with the values of Θ in the range of +2– +41 K. The temperature dependence of the susceptibility of $Cu(NCO)_2$(o-tol)$_2$ conforms with a one-dimensional Ising model for g = 2.12 and 2J = –20 cm^{-1}.

Introduction

In studying[3] the spectral properties of new complexes of the type $Cu(NCO)_2L_2$ where L is a ligand of the aniline group we have obtained some basic knowledge of their molecular structure and the bonding mode of the cyanate group. In order to gain further information especially concerning any intermolecular interactions which could occur in the crystal structures, we have recorded the ESR spectra of these complexes and measured their magnetic susceptibilities at different temperatures. It has been shown that most of the ESR spectra are rather unusual and help together with the magnetic susceptibility data to recognize the influence of variously substituted anilines on the structural characterization of the complexes. Therefore we report the results of our research herein; a preliminary communication on the magnetic moments, except for $Cu(NCO)_2$(p-bromoan)$_2$, is in ref.4.

Experimental Section

The ESR spectra were recorded using a Varian E–3 apparatus operating at X band frequency with 100 kHz modulation. The material for the measurements was taken in crystalline powder form.

The magnetic susceptibilities were measured by the Gouy method as described previously.[5] The susceptibility of $Cu(NCO)_2$ (o-tol)$_2$ was also measured in the course of a continuous temperature increase, from 77 K up to 288 K, at a field strength of 9.8 kOe, on an apparatus of the Institute of Chemistry, University of Wroclaw. The molar susceptibilities were corrected for the diamagnetism of the constituents using Pascal's constants[6] and the effective magnetic moments were calculated from the relation

$$\mu_{eff} = 2.83\ [(\chi_M^{corr}–N\alpha)T]^{1/2}$$

where for the temperature-independent paramagnetism, $N\alpha$, the value of 60×10^{-6} c.g.s.u./mole[7] was inserted.

Results and Discussion

ESR Spectra

The derivative ESR spectra were analysed by Kneubühl's method[8] and the obtained g factor values are presented in Table I. Some selected spectra are shown in Figure 1.

All the complexes under investigation give anisotropic ESR spectra from which the average g factor values, g_o, follow in the range of 2.122 ± 0.013, being in agreement[9] with an orbitally non-degenerated ground state. Since the crystal structures of these complexes are not known, we cannot conclude[10] to what extent the found crystal g values reflect the concerned molecular symmetries. Three cases are worth of particular consideration.

$Cu(NCO)_2(an)_2$ exhibits an essentially orthorhombic ESR spectrum but the g_2 value is only poorly resolved and is numerically very close to g_1. If the value

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* Dedicated to Professor Z. Valtr on the occasion of his 60th birthday.

TABLE I. Crystal g values of $Cu(NCO)_2L_2$ complexes.

L	g_1	$g_\perp$	g_2	$g_\parallel$	g_3	$g_o{}^a$
an	2.050		2.077		2.229	2.119
p-chloroan	2.054		2.137		2.192	2.128
p-bromoan	2.044		2.119		2.179	2.114
p-iodoan		2.176		2.054		2.135^b
		2.167^c		2.048^c		$2.127^{b,c}$
o-tol		2.043		2.251		2.112^b
m-tol	2.051		2.125		2.190	2.122
p-tol	2.053		2.136		2.190	2.126

[a] Calculated by the relation $g_o = \frac{1}{3}(g_1 + g_2 + g_3)$ or [b] $g_o = \frac{1}{3}(2g_\perp + g_\parallel)$. [c] Measured at −140° C.

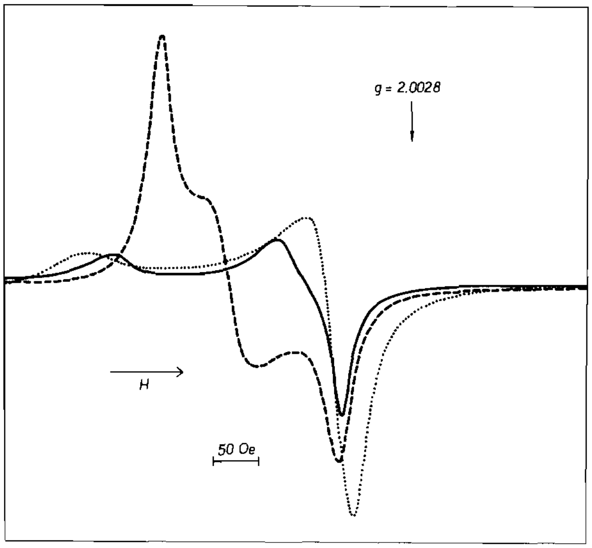

Figure 1. ESR spectra of $Cu(NCO)_2(an)_2$ (——), $Cu(NCO)_2(p\text{-}tol)_2$ (– – –), and $Cu(NCO)_2(o\text{-}tol)_2$ (· · ·).

of the parameter G defined[11] by the ratio $(g_{//} -2)/(g_\perp -2)$ is calculated using both extreme g values, a value of 4.58 is obtained. Such a value (>4) may be expected[11] for tetragonal systems of $Cu^{(II)}$ with a d_{x2-y2} ground state, assuming that the tetragonal axes are aligned parallel and the local g values are not affected by exchange coupling. An elongated tetragonal stereochemistry of $Cu(NCO)_2(an)_2$ is strongly corroborated also by the spectral results.[3] The observed small $g_\perp$ anisotropy possibly indicates the occurrence of a weak rhombic component which most likely arises due to some distortions in the xy plane.

Complexes with L = p-chloroan, p-bromoan, m-, and p-tol give orthorhombic ESR spectra and the corresponding g values are rather consistent. These spectra are of the "reversed" type[10] considering the line for the highest g value is of higher intensity than that for the lowest one. In the case of $Cu(NCO)_2(p\text{-}iodoan)_2$ the ESR spectrum is axial, its shape indicates[11] exchange interaction and is also "reversed",[10] i.e. $g_{//} > g_\perp$; this feature becomes somewhat more pronounced at −140° C.

Since on the basis of the spectral results[3] a tetragonal stereochemistry involving a d_{x2-y2} ground state is likely to be maintained for all above compounds, we tentatively suppose that their unit cells contain[12] two sets of crystallographically non-equivalent molecules $Cu(NCO)_2L_2$ (ref.3), whose principal axes are inclined at about 90° to one another. Thus, appreciable exchange coupling[13] between non-equivalent copper(II) ions takes place resulting in the observed crystal g values. This contigence is evidenced[10] by the observed "narrowing" of the extreme g values which could be of exchange origine and in accordance with that also the temperature dependence of the magnetic moments has been found for the complexes with L = p-chloroan, p-bromoan, m-, and p-tol. It is clear that a rearrangement of the crystallographic symmetry, without any substantial change in the stereochemistry, is quite acceptable, since it would be caused by the bonding of the p- and m-substituted anilines, respectively, instead of aniline alone.

$Cu(NCO)_2(o\text{-}tol)_2$ exhibits an axial ESR spectrum of a "normal" type, but the G value is surprisingly high, i.e. 5.84. It indicates[11], however, that exchange interaction, as revealed by the temperature dependence of the magnetic moment, occurs between crystallographically equivalent copper(II) ions. Thus, the found g values may be considered to be the true values of the local environment of the copper(II) ion. Any reduction of the microsymmetry being probable for the structure suggested on the basis of the magnetic susceptibility (see bellow), might cause[14] some shift of the g values leading to the observed high value of G.

Magnetic Susceptibilities

The results of the magnetic susceptibility measurements are listed in Table II. From the plots demonstrating the validity of the Curie–Weiss law in the form of $1/(\chi_M{}^{corr} - N\alpha) = T/C + \Theta/C$, the Curie constants C and the Weiss constants Θ were determined as

TABLE II. Magnetic data of $Cu(NCO)_2L_2$ complexes at various temperatures. All susceptibilities are in 10^{-6} c.g.s.u./mole, magnetic moments are in B.M.

L	Diamagn. Corr.	Temperature (K)								C (c.g.s.u. K/mole)	Θ (K)
		293		273		201		82			
		χ_M^{corr}	μ_{eff}	χ_M^{corr}	μ_{eff}	χ_M^{corr}	μ_{eff}	χ_M^{corr}	μ_{eff}		
an	−179	1498	1.84	1564	1.81	2105	1.81	5293	1.85	0.420	+2
p-chloroan	−213	1502	1.84	1598	1.83	2073	1.80	4462	1.70	0.457	+23
p-bromoan	−234	1497	1.84	...	...	2141	1.83	4889	1.78	0.433	+8
p-iodoan	−262	1562	1.88	1638	1.86	2218	1.87	5240	1.85	0.441	+3
m-tol	−201	1515	1.85	1627	1.85	2068	1.80	4566	1.72	0.454	+18
p-tol	−195	1487	1.83	1588	1.83	2077	1.80	4540	1.71	0.440	+16

L = o-tol
Diamagn. Corr. = −202

T(K)	293	288	273[a]	259	246	233	221	210	198	186	151	140	103	77
χ_M^{corr}	1396	1436	1480	1549	1610	1686	1751	1806	1900	1998	2352	2530	3181	3967
μ_{eff}	1.77	1.78	1.76	1.76	1.75	1.74	1.73	1.71	1.71	1.70	1.66	1.66	1.60	1.55

C = 0.445 c.g.s.u.K/mole
Θ = +41 K

[a] Below this temperature only the results of continuous susceptibility measurement are included.

the reciprocal slopes of the straight lines and the negative intercepts on the temperature axis.

In the case of the complexes with L = an, p-chloroan, p-bromoan, p-iodoan, m-, and p-tol the Weiss constants are in the range of +2– +23 K. With respect to the insignificant Θ values of the complexes with L = an and p-iodoan, Curie rather than Curie–Weiss behaviour may be assigned to them. Consequently the magnetic moments for these two complexes are practically temperature independent, while those for the former compounds are slightly reduced with decreasing temperature. Since the occurrence of a degenerated ground state may be securely precluded, evidently slight exchange demagnetisation takes place in the respective complexes. As we already have pointed out in the ESR section, this is probably conditioned by the packing in the crystal structure, where the cyanate group may be an applicable medium for the spin transmission between the adjacent paramagnetic ions.

It is noteworthy that the values of Θ appreciably decrease in the order of the complexes with L = p-chloroan > p-bromoan > p-iodoan, so that exchange interaction diminishes in the same order; in $Cu(NCO)_2$ (p-iodoan)$_2$ it is distinctly observable only in the ESR spectrum (see earlier). We are inclined to suggest that this fact is connected with the bulkiness of the halogen in the L molecule, by which the magnetic insulation of the adjacent molecules in the crystal structure is enlarged.

The susceptibility of $Cu(NCO)_2$(o-tol)$_2$ also obeys the Curie–Weiss law (Figure 2), but the Weiss constant amounts to +41 K. Therefore the magnetic moment, being still "normal" at room temperature, is reduced with decreasing temperature. This magnetic behaviour obviously shows the presence of definite antiferromagnetic interaction between the copper(II) ions in a suitable bonding system. This enables us to suppose a polynuclear chain structure, in which the copper(II) ions are bridged by the nitrogen atoms of the cyanate groups (Figure 3). The bridging function of these groups is quite in accordance with the IR spectral results.[3] An alternative mode of bridging, *via* both the nitrogen and oxygen of the cyanate groups, seems to be not attractive because of a reluctance of these groups to the bonding through the oxygen.[16] Furthermore, an N, O bridging would yield rather a long and intricate pathway for the spin interaction within the chains, so that a considerably weaker antiferromagnetism would result. An antiferromagnetic behaviour with a similar value of Θ was observed[17] for $Mn(NCO)_2$(3-Cp)$_2$ and $Mn(NCO)_2$(4-Cp)$_2$ (Cp= cyanopyridine) which by IR spectral evidence exhibit NCO bridges and nitrogen bridging is also preferred.

Considering that the assumed structure of Cu $(NCO)_2$(o-tol)$_2$ consists of linear chains of copper (II) ions, it seems convenient to apply the anisotropic Ising model[18] to the temperature dependence of its susceptibility. According to this model the temperature dependence of the susceptibility of a linear antiferromagnet represented by a chain of Ising spins with S = 1/2 in the region above the Néel temperature follows equation (1)

$$\chi_M^{corr} = \frac{N\beta^2 g^2}{4kT} \exp\,(2J/kT) + N\alpha \qquad (1)$$

where J is the exchange interaction energy (the

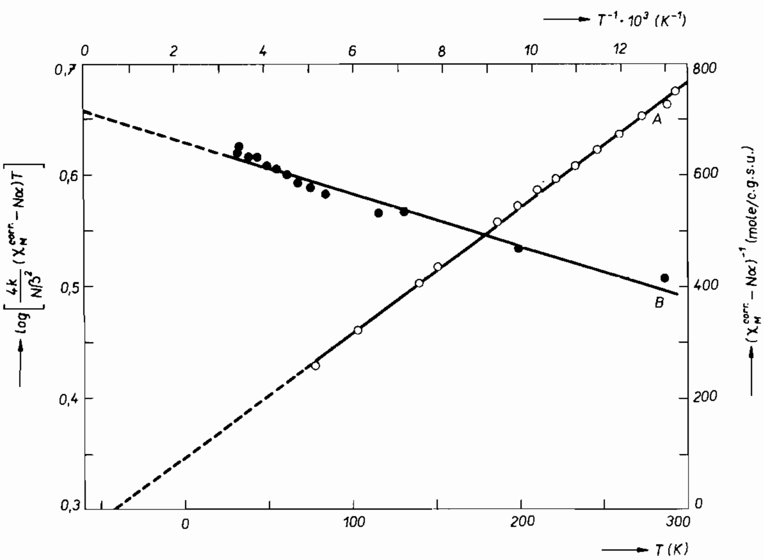

Figure 2. The dependence of the reciprocal magnetic susceptibility against the temperature (A) and log $[4k(\chi_M^{corr} - N\alpha)T/N\beta^2]$ against the reciprocal temperature (B) for $Cu(NCO)_2(o\text{-}tol)_2$.

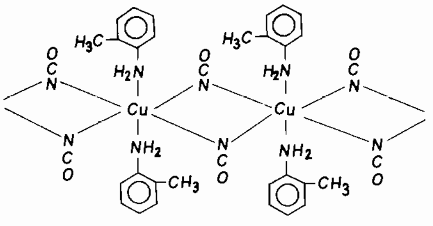

Figure 3. The assumed structure of $Cu(NCO)_2(o\text{-}tol)_2$.

exchange integral); the meaning of the other symbols is evident. Equation (1) may be readily converted into its logarithmic form (2).

$$\log \frac{4k(\chi_M^{corr} - N\alpha)T}{N\beta^2} = 2 \log g + (2J/2.303k)T^{-1} \quad (2)$$

The dependence of $\log[4k(\chi_M^{corr} - N\alpha)T/N\beta^2]$ against T^{-1} is linear and that one for our complex is plotted in Figure 2. The points obtained from the experimental susceptibilities lie, within an experimental inaccuracy,[19] on a straight line proving the validity of the Ising model. The slope of the straight line gives for the energy separation between a singlet and a triplet level, 2J, the value of $-20\ cm^{-1}$ ($\pm\ 3\ cm^{-1}$). This value is near to that of $-16\ cm^{-1}$ ($\pm\ 3\ cm^{-1}$) calculated[4] from the magnetic moments at three different temperatures using the ESR value of g. The ordinate of the crossing point of the straight line with the vertical axis yields the g value of 2.12($\pm$0.03). It is somewhat lower than that following from the Curie constant and amounting to 2.17($\pm$0.02), yet it agrees excellently with the average g value of 2.11, found from the ESR spectrum and thus being most reliable. For the temperature of maximum susceptibility $T_m = -2J/k$ the value of 29 K appears which is comparable with that of Θ, 41 K, since for $kT \gg 2J$, Θ would be $\approx T_m$ (ref.20).

We suppose that the antiferromagnetism of $Cu(NCO)_2(o\text{-}tol)_2$ is caused by superexchange interaction the mechanism of which already hat been briefly discussed.[4]

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