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Physical Properties and Structure of Potassium Tricyanatocuprate(II)

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Tsivadze *et al.* measured [1] the infrared spectrum of $KCu(NCO)_3$ and established an unusually manifold splitting of the vibrational bands of the NCO group. On this basis they claimed that both the terminally N-bonded and the bridged NCO groups are present. Nevertheless, Bailey *et al.* regarded [2] the spectrum as questionable because of the large number of peaks. Therefore and since $KCu(NCO)_3$ is one of the fundamental cyanate complexes of copper(II), some more detailed knowledge of its structure seems desirable. Since till now we did not succeed in preparing single crystals of this compound, we have carried out the structural research using a number of physical methods.

Experimental

The compound was prepared according to the procedure used [3] by Söderbäck (Calc.: C, 15.76; N, 18.37; Cu, 27.78. Found: C, 15.60; N, 18.30; Cu, 27.72%).

The solid state electronic [4], infrared [5] and ESR spectra [6], and the magnetic susceptibilities [5] were obtained as described in the cited papers.

Results and Discussion

The solid state electronic spectrum exhibits a broad ligand field band with a maximum at 1.36 μm^{-1} and a pronounced shoulder at ≈ 0.70 μm^{-1}. This type of d ← d spectrum agrees [7] very well with a distorted tetrahedral arrangement of the donor nitrogen atoms. In the high wavenumber region a shoulder at ≈ 2.37 μm^{-1} occurs, originating from some charge transfer transition, most likely of the ligand to metal type.

The infrared spectrum is in overall pattern consistent with that found [1] by Tsivadze *et al.* The frequencies of the NCO fundamentals and the far infrared vibrations (down to 200 cm^{-1}) are listed in Table I. The spectrum still contains several weak or very weak bands, not included in Table I, apparently combinations or overtones in origin.

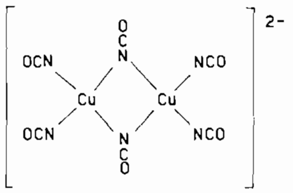
TABLE I. Infrared Frequencies (cm^{-1}).[a]

ν_{as}(NCO)	ν_s(NCO)	δ(NCO)	ν(Cu–NCO)	Other Bands
2268vs	1342ms	698ms	354s[c]	263m
2252vs	1312m[b]	656s		242m
2215vs	1288mw[b]	637s		≈205s
2164sh		612sh		
2152s		606s		

[a] s = strong, m = medium, w = weak, v = very, sh = shoulder.
[b] The assignment 2δ(NCO) is also possible.
[c] Unresolved splitting appears; the average frequency is given.

The predicted [1] presence of terminally bonded as well as of bridged NCO groups gives rise to two ν_{as}(NCO) stretches, each of them being split due to a low symmetry of the CuN_4 skeleton. Similarly it should be with the ν_s(NCO) mode, but the real situation is here less easy to survey. Again, separated δ(NCO) modes may be attributed to each kind of NCO groups. In addition the NCO bridging *via* the nitrogen atom causes [8] a great splitting of the respective mode, well above 50 cm^{-1}. In the far infrared region only one band is assignable [9, 10] to the ν(Cu–NCO) stretch. This is, however, broad and exhibits an unresolved splitting. Two bands in the vicinity of 250 cm^{-1} correspond [10] very likely to the split Cu–NCO deformation mode (though one band at 252 cm^{-1} was reported in the work [9]).

From the foregoing results it may be reasonably supposed that the complex anion possesses a binuclear structure, displaying a pseudotetrahedral symmetry around each Cu(II) atom:



The magnetic susceptibilities (Table II) were fitted to the Curie–Weiss law $\chi_M = C(T + \theta)^{-1}$ using the nonlinear least squares method by a minimization of the value $S = \Sigma_{i=1}^{n} [\chi_M(expt)_i - \chi_M(calc)_i]^2$ applying the method of Fletcher and Powell [11]. The best parameter values are C = 0.507 ± 0.004 c.g.s.u. $kmol^{-1}$ and $\theta = -(9.2 \pm 0.7)$ K [12]. Although the high room temperature magnetic moment could be caused by a pseudotetrahedral stereochemistry presumed, its temperature dependence does not agree with this case [13]. To our mind a ferromagnetic interaction between adjacent Cu(II) atoms takes place, yielding a spin triplet as the ground state.

TABLE II. Magnetic Properties.

T(K)	$10^6\chi_M$(expt) (c.g.s.u. mol^{-1})	μ_{eff}(expt)[a] (B.M.)	$10^6\chi_M$(calc)[b] (c.g.s.u. mol^{-1})	μ_{eff}(calc)[a] (B.M.)
294	1744	2.025	1739	2.02
252.8	2044	2.03	2053	2.04
223.1	2350	2.05	2356	2.05
193.4	2771	2.07	2755	2.06
163.7	3297	2.08	3303	2.08
143.9	3800	2.09	3796	2.09
124.1	4443	2.10	4446	2.10
104.3	5330	2.11	5339	2.11
94.4	5929	2.12	5922	2.115

[a] Calculated from the relation $\mu_{eff} = 2.828(\chi_M T)^{1/2}$. [b] Calculated from equation (1) using the best fitted parameters quoted in the text.

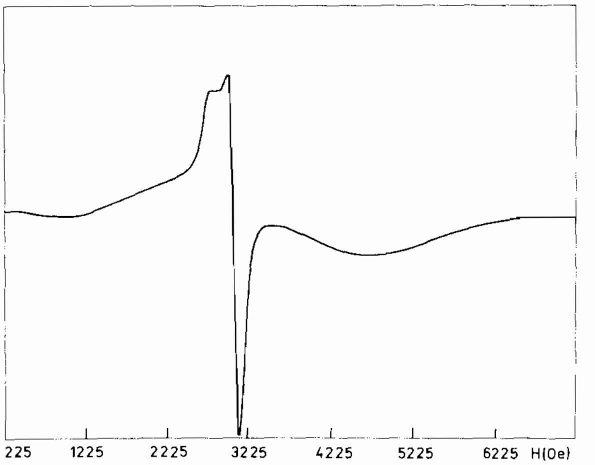


Fig. 1. ESR spectrum of powdered $KCu(NCO)_3$.

Since the existence of the dimeric $[Cu_2(NCO)_6]^{2-}$ systems seems very probable, we tried to fit the experimental susceptibilities to the Bleaney–Bowers equation [14] for pairwise coupled Cu(II) atoms (1), where the symbols have their usual meanings.

$$\chi_M = \frac{g^2N_A\beta^2}{3kT}\,[1 + 1/3\exp(-2J/kT)] + N_A\alpha \qquad (1)$$

$-2J$ is the energy separation between the singlet and triplet state. The fitting procedure similar to that described above led to the parameters $J = 110 \pm 8$ cm^{-1}, $g = 2.124 \pm 0.002$ and $N_A\alpha = (17 \pm 17) \times 10^{-6}$ c.g.s.u. mol^{-1}. The standard deviation of $N_A\alpha$ indicates that in our case this parameter is of no physical meaning. The sum of the squares of the deviations is 5.8×10^{-10}. The coincidence between the experimental susceptibilities and those calculated using equation (1) is excellent, as can be seen from Table II. It is also noteworthy that, according to our results, the $[Cu_2(NCO)_6]^{2-}$ anion is one of the strongest intramolecular ferromagnets.

The ESR spectrum of the powdered material (Figure 1) is similar to the spectra observed [15] by Hatfield *et al.* for the dimeric hydroxo-bridged copper(II) complexes of 2,2′-dipyridyl, in which the Cu(II) atoms are exchange coupled. Our spectrum contains a weak broad band at about 920 Oe, a sharp intense line near 3050 Oe and a very broad, less intense band centred at about 4725 Oe. Following the work [15], we are able to assign the last absorption to the $\Delta M_S = 1$ high field perpendicular transition. The assignment of the first absorption is not unambiguous, but we believe it to be connected with the forbidden $\Delta M_S = 2$ transition rather than with the $\Delta M_S = 1$ low field parallel transition. The $\Delta M_S = 1$ low field perpendicular and high field parallel transitions are not resolved in the given spectrum. The 3050 Oe band apparently originates from a relatively large amount of monomeric copper(II) species present in the main substance as impurities.

The exchange coupling proved may be propagated through an ≈ 90° Cu–N–Cu pathway involving the σ-orbitals of the interacting atoms, similarly as it has been discussed elsewhere [16].

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