(23) D. J. Brauer and C. Krüger, *J. Organomet. Chem.*, **77**, 423 (1974).
(24) J. K. Stalick and J. A. Ibers, *J. Am. Chem. Soc.*, **92**, 5333 (1970).
(25) R. A. Schunn, *Inorg. Chem.*, **15**, 208 (1976).
(26) J. C. Huffman, W. E. Streib, and C. R. Sporleder, unpublished results.

Contribution from the Departments of Chemistry, Western Washington University, Bellingham, Washington 98225, and Washington State University, Pullman, Washington 99163

Magnetic Exchange in a One-Dimensional Polymeric Chain Containing Cyanide-Bridged Copper(II)

C. P. Landee,[1a] M. Wicholas,*[1b] R. D. Willett,*[1a] and T. Wolford[1b]

Received December 8, 1978

Although cyanide rapidly reduces copper(II) to copper(I) when mixed together in aqueous solution,[2] it has recently been shown possible to isolate stable ternary copper(II) complexes containing coordinated cyanide and nitrogen donor bases.[3] This communication discusses the interaction of copper(II), 2,2′,2″-terpyridine (terpy), and cyanide, the isolation of two stable complexes [Cu(terpy)CN]NO_3·H_2O and [Cu(terpy)-CN]ClO_4, and their magnetic properties.

Magnetic interactions in these complexes should be of interest being that [Cu(terpy)CN]NO_3·H_2O is a one-dimensional polymeric chain containing cyanide, which bridges between adjacent copper(II) ions[4] whose unpaired spins should be in near-orthogonal molecular orbitals. Such chains ideally should be ferromagnetic and only one example of a one-dimensional ferromagnetic $S = {}^1/_2$ chain is presently known.[5]

Experimental section

Synthesis of [Cu(terpy)CN]X. X = ClO_4^-. A 0.100-g (4.3×10^{-4} mol) portion of terpy was dissolved with heating in a 20-mL aqueous solution containing 0.092 g (4.3×10^{-4} mol) of $Cu(NO_3)_2$·$3H_2O$. An aqueous solution (8 mL) of KCN (0.028 g, 4.3×10^{-4} mol) was added dropwise with stirring to the aforementioned hot solution, and this was followed by 5 mL of aqueous $NaClO_4$ (0.053 g, 4.3×10^{-4} mol). Blue crystals of product separated, were washed with ice-cold water, and were dried over P_2O_5 for 24 h. Anal. Calcd for [Cu-($C_{15}H_{11}N_3$)CN]ClO_4: C, 45.51; H, 2.63; N, 13.26. Found: C, 45.54; H, 2.59; N, 13.31.

X = NO_3^-. Blue crystals of the complex [Cu(terpy)CN]NO_3·H_2O were isolated as previously described.[4]

Infrared spectra were run on a Perkin-Elmer 521 and magnetic susceptibilities were determined from 1.7 to 100 K by using a PAR vibrating sample magnetometer as previously described.[6]

Results and Discussion

An initial plot of $1/\chi$ vs. T for the NO_3^- salt indicated Curie–Weiss behavior with an intercept of approximately −1 K, thus showing the presence of weak antiferromagnetic interaction. A more sensitive indication of the antiferromagnetic nature of the magnetic exchange is obtained from a plot of χT vs. T (Figure 1), as shown by the decrease of χT at low temperature. Because of the linear chain structure of the salt, the data were fit to the high-temperature series expansion of Baker et al.[7] for the $S = {}^1/_2$ Heisenberg antiferromagnet. The results of the least-squares analysis of the data are shown as the solid line in Figure 1, with $J = -0.44$ cm^{-1} and $g = 2.087$. A comparable, although somewhat poorer, fit could also be obtained from the $S = {}^1/_2$, Ising model predictions[8] with $J = -0.53$ cm^{-1} and $g = 2.105$. However, because of the nearly isotropic **g** tensor for Cu^{2+} salts, the Heisenberg model is more appropriate, and the value of $J = -0.44$ cm^{-1} is to be preferred.

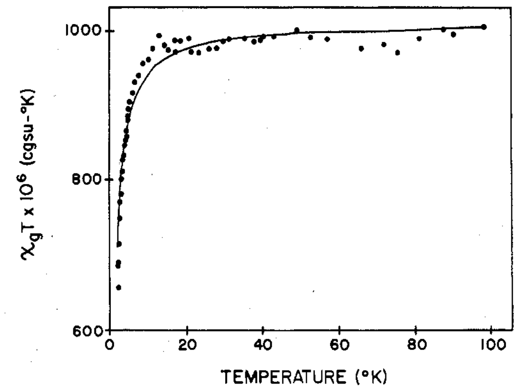

Figure 1. Plot of the function $\chi_g T$ vs. temperature for [Cu(terpy)CN]NO_3·H_2O. The dots represent the experimental values; the solid line represents the best least-squares fit.

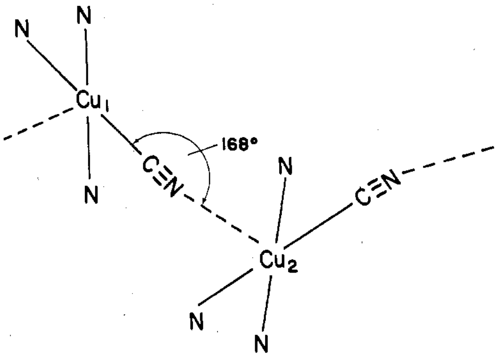

Figure 2. Geometry of the one-dimensional polymeric chain, [Cu-(terpy)CN]NO_3·H_2O.

Table I. Exchange Coupling Constants and Structural Parameters for Cyanide-Bridged Copper(II)

compound[a]	J, cm^{-1}	structure[b]	cyanide bridging[c]
[Cu(terpy)CN]NO_3·H_2O	−0.44	SPY	(e,a)
[$Cu_2(bpy)_4CN$]$(PF_6)_3$[d]	−9.4	TBP	(e,e)
[$Cu_2(phen)_4CN$]$(PF_6)_3$[d]	−29	TBP	(e,e)
[$Cu_2(tren)_2CN$]$(PF_6)_3$[d]	−88	TBP	(a,a)
[Cu_2([14]4,11-diene-N_4)$_2$CN]$(ClO_4)_3$[e]	−4.8	TBP	(e,e)

[a] bpy = 2,2′-bipyridine; phen = 1,10-phenanthroline; tren = 2,2′,2″-triaminotriethylamine; [14]4,11-diene-N_4 = 5,6,6,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene. [b] Key: TBP = trigonal bipyramidal; SPY = square pyramidal. [c] Key: a = axial; e = equatorial; (e,a) represents (C bond, N bond). [d] Reference 9. [e] Reference 8.

In our discussion of the mechanism of superexchange responsible for $J = -0.44$ cm^{-1}, the structure of [Cu(terpy)-CN]NO_3·H_2O should first be mentioned here. Each copper(II) is in a square-pyramidal environment with the terpyridine nitrogen and cyanide carbon bonding equatorially; the apical position is occupied by a cyanide nitrogen which bridges from an adjacent Cu(terpy)CN^+ unit.[4] This is qualitatively illustrated in Figure 2.

The very weak antiferromagnetic coupling observed in [Cu(terpy)CN]NO_3·H_2O may be compared with the antiferromagnetic exchange interactions occurring in the four other known cyanide-bridged copper(II) complexes listed in Table I. The four complexes studied by Hendrickson[9,10] all have trigonal-bipyramidal geometry and an anticipated d_{z^2} ground state for copper(II). In each case antiferromagnetic superexchange can be rationalized by invoking overlap of d_{z^2} with σ orbitals on CN^-. For [Cu(terpy)CN]NO_3·H_2O, the anticipated ground state is $d_{x^2-y^2}$. Considering for simplicity the qualitative structure shown above, we find the $d_{x^2-y^2}$ orbital on Cu_1 has a symmetry-allowed overlap with the highest filled σ MO on cyanide. The latter however is essentially orthogonal to $d_{x^2-y^2}$ on Cu_2, and hence sizable antiferromagnetic super-

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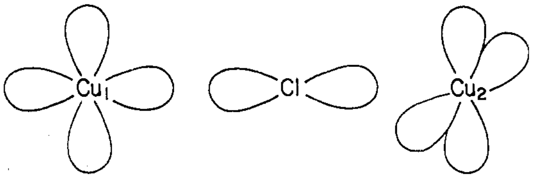

Figure 3. Orbital overlap scheme for the chloride bridging in $(RNH_3)_2CuCl_4$.

exchange coupling is vitiated here in contrast to the four other cyanide-bridged species.

The magnetic behavior of [Cu(terpy)CN]NO_3 may also be compared with that in the linear halide bridged, two-dimensional, ferromagnetic $(RNH_3)_2CuCl_4$ and $(RNH_3)_2CuBr_4$ salts[11] (Figure 3). The similarity here is that the bridging angle in both cases ideally should be 180°. In these latter salts, the unpaired electron density on Cu_1 is delocalized onto a p orbital on the bridging halide.[12] Thus, as in [Cu(terpy)CN]NO_3·H_2O, it is in an orbital orthogonal to the $d_{x^2-y^2}$ orbital on Cu_2 and Hund's rule leads to the prediction of the observed, ferromagnetic interaction ($J \sim +10$ cm^{-1}) via this one-atom bridge. A similar bridging mechanism can be proposed for [Cu(terpy)CN]NO_3·H_2O wherein unpaired electron density is delocalized into a σ^* molecular orbital resulting from the interaction of $d_{x^2-y^2}$ on Cu_1 with the highest filled σ orbital on cyanide. Were the resulting molecular orbital strictly orthogonal to $d_{x^2-y^2}$ on Cu_2, ferromagnetic exchange coupling would result. However, bending of the Cu_2NC angle away from 180° could produce slight antiferromagnetism. Since the angle in question is 164°,[4] the observed weak antiferromagnetism of [Cu(terpy)CN]NO_3·H_2O may very well be a consequence of the nonlinear bridge.

Evidence as to the weakness of cyanide bridge can be found from the infrared spectrum of [Cu(terpy)CN]NO_3·H_2O. Whereas the Nujol mull spectrum shows a CN stretching mode at 2171 cm^{-1} as expected for bridging cyanide,[10] the same band shifts to 2143 cm^{-1} when pelleted in KBr. In the latter instance the CN bridge is surely broken under high pressure to give a terminal cyanide linkage. This underscores the danger of relying solely on KBr pelleting as a means of deducing structural information from infrared spectra.

Although one might expect [Cu(terpy)CN]ClO_4, to be analogous in structure and magnetic properties to the NO_3^- complex, this seems not to be the case. The infrared spectrum shows a cyanide stretching band at 2145 cm^{-1} (Nujol mull) and a somewhat split ν_3 band for ClO_4^- at 1084 and 1112 cm^{-1}. Also, the complex exhibits linear Curie–Weiss behavior in the temperature range 1.7–100 K with $\Theta = -0.026$ K. With this small value for the Weiss constant, no further analysis was made on this basically paramagnetic salt. Hence both the infrared and magnetic data combined imply monomeric copper(II) with terminal cyanide and possible weak interaction of copper(II) with ClO_4^-. Quite likely, the cyanide bridging found in [Cu(terpy)CN]NO_3·H_2O but absent in the ClO_4^- salt, may be due to a difference in lattice forces within the two salts.

Acknowledgment. The authors acknowledge the National Science Foundation for award of a research grant to R.D.W., the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research through a grant to M.W., and the M. J. Murdock Charitable Trust Grant of Research Corp.

Registry No. [Cu(terpy)CN]ClO_4, 70235-90-4; [Cu(terpy)CN]NO_3, 70235-91-5.

References and Notes

(1) (a) Washington State University. (b) Western Washington University.
(2) A. G. Sharpe, "The Chemistry of Cyano Complexes of the Transition Metals", Academic Press, New York, 1976, p 266.
(3) M. Wicholas and T. Wolford, *Inorg. Chem.*, **13**, 316 (1974).
(4) O. P. Anderson, A. B. Packard, and M. Wicholas, *Inorg. Chem.*, **15**, 1613 (1976).
(5) C. P. Landee and R. D. Willett, submitted for publication in *Phys. Rev. Lett.*
(6) C. P. Landee, S. A. Roberts, and R. D. Willett, *J. Chem. Phys.*, **68**, 4574 (1978).
(7) G. A. Baker, Jr., G. S. Rushbrooke, and H. Gilbert, *Phys. Rev.*, **135**, 1272 (1964).
(8) J. W. Stout and R. C. Chisholm, *J. Chem. Phys.*, **36**, 979 (1962).
(9) D. M. Duggan, R. G. Jungst, K. R. Mann, G. D. Stucky, and D. N. Hendrickson, *J. Am. Chem. Soc.*, **96**, 3443 (1974).
(10) D. S. Bieksza and D. N. Hendrickson, *Inorg. Chem.*, **16**, 924 (1977).
(11) L. J. deJongh and A. R. Miedema, *Adv. Phys.*, **23**, 1 (1974).
(12) C. Chow, K. Chang, and R. D. Willett, *J. Chem. Phys.*, **59**, 2629 (1973).

Contribution from the Department of Chemistry,
Southampton University, Southampton, United Kingdom

Methyltrioxorhenium. An Air-Stable Compound Containing a Carbon–Rhenium Bond

Ian R. Beattie* and Peter J. Jones

Received March 7, 1978

During the preparation of trimethyldioxorhenium (using literature methods[1]), we observed the growth of needle crystals in tubes containing residues and which had been left open to the atmosphere. Purification of the product by sublimation in vacuo resulted in the isolation of a colorless crystalline material which melted sharply. Elemental analysis suggested the compound to be methyltrioxorhenium. The compound could be synthesized by exposure of either tetramethyloxorhenium[2] or trimethyldioxorhenium[1] to dry air in a closed system. The mass spectrum showed parent-ion peaks $CH_3ReO_3^+$ at 250 and 248 mass units corresponding to species containing ^{187}Re and ^{185}Re, respectively. The two peaks did not have the expected intensity ratio based on the relative isotopic abundances, due to the overlap of the lower mass unit peak with that of the species $CH^{187}ReO_3^+$.

Experimental Section

Approximately 100 mg of Me_4ReO[2] (Me = methyl) or Me_3ReO_2[1] was transferred into a 1-L bulb. Dry air was admitted up to atmospheric pressure. The growth of long needles could be seen in a few days, and after 4 weeks yields in excess of 50% were obtained. The product was purified by sublimation in vacuo. $MeReO_3$ is soluble in CH_3CN, C_6H_6, $CHCl_3$, EtOH, or Et_2O (Et = ethyl). It is also sparingly soluble in CS_2 or C_6H_{14}. The proton magnetic resonance spectrum in $CDCl_3$ showed one sharp resonance at τ 7.4. (This value is close to that found for related methylrhenium compounds.[1,2]) Elemental analysis for C and H gave the following. Anal. Calcd for CH_3O_3Re: C, 4.82; H, 1.20. Found: C, 4.94, 4.98; H, 1.26, 1.25. The melting point was 110 °C.

Results and Discussion

The vibrational spectra under a variety of conditions are summarized in Table I. The assignments are based on a "tetrahedral" monomeric species with a direct rhenium–carbon bond. The results are comparable to those obtained for ReO_3Cl[3] and (monomeric) ReO_3F.[4] The rhenium–carbon bond stretching mode is expected to occur in the region of 500 cm^{-1}.

Two features of this compound are of particular interest: the presence of a rhenium–carbon bond in an air-stable compound and the stabilization of a rhenium–carbon bond by the oxo ligands. The possibility that this material might be methyl perrhenate is eliminated by its stability to water. In 1974 it was pointed out[5] that the only known ester of perrhenic acid is the trimethylsilyl derivative, and this is (as expected) very sensitive to hydrolysis.[6] Finally, we note that the preparation of this compound suggests that suitable preparative

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