Correspondence

The Nonexistence of Pentacoordinate Dichlorotris(thiourea)cobalt(II), $Co(tu)_3Cl_2$[1]

Sir:

In 1966 Dash and Rao[2] reported blue complexes of the type $Co(tu)_3X_2$ [tu = thiourea; X = Cl, Br]. On the basis of analysis, magnetic moments, visible spectra, and conductance measurements they assigned to these tris complexes high-spin pentacoordinate CoS_3X_2 structures. The method of preparation, color, and the published spectra[2] of the complexes correspond closely to those reported earlier by Cotton, *et al.*,[3] for the tetracoordinate pseudotetrahedral $Co(tu)_2X_2$ bis complexes. These factors prompted us to undertake a reinvestigation of the system.

The syntheses of the bis and tris complexes by the literature methods,[2,3] which differ from one another only in the solvent used (1-butanol for the bis and ethanol followed by chloroform for the tris compounds) and minor details of quantity, were accomplished with excellent analyses obtained (Table I) in each case. The two series of complexes were then subjected to study by a variety of physical methods with the results presented below.

The electronic spectra recorded on acetone solutions were identical on a molar basis for the bis and tris chloride and bromide complexes, respectively, and agreed with the results of Cotton, *et al.*,[3] for the $Co(tu)_2X_2$ compounds, indicating that the chromophore was the pseudotetrahedral $Co(tu)_2X_2$ moiety in each instance. The electronic mull spectra for the corresponding bis and tris complexes were identical to within experimental error. Likewise the infrared spectra recorded on Nujol mulls in the 200–1350-cm^{-1} region were indistinguishable with regard to band frequencies, but slight differences in some of the relative intensities were observed between corresponding bis and tris compounds. Molecular weights determined in acetone solution were roughly equal to the calculated formula weight for the bis compounds and about half of this quantity in the case of the tris samples (Table I). At this point a *working hypothesis* consistent with the above observations was formulated, namely, that the tris compounds were lattice complexes of $Co(tu)_2X_2$ and an uncoordinated molecule of tu. Upon dissolution in acetone of 1 mol of such a complex 1 mol of $Co(tu)_2X_2$ and 1 mol of tu would result and this would account for the spectroscopic and molecular weight data and would be consistent with the observed[2] lack of ionic conductance in solution.

A single-crystal X-ray structure determination was undertaken on the tris chloride compound in order to test the foregoing hypothesis. A batch of crystals was prepared by recrystallization from acetone (analytical and molecular weight data on this batch were virtually identical with those of the unrecrystallized material; see Table I). Two types of blue crystal were picked out of this batch: monoclinic crystals with $a = 8.154$ (5) Å, $b = 11.817$ (5) Å, $c = 10.845$ (5) Å, $\beta = 103.78$ (5)°, $V = 1014.9$ Å^3 (diffractometer data) and tetragonal crystals with $a = 13.50$ (5) Å, $c = 9.12$ (5) Å, $V = 1664$ Å^3 (film data). The density of material in this sample was measured by flotation in diiodomethane–carbon tetrachloride and found to be 1.85 (1) g/cm^3. No integral number of formula units of tris complex consistent with this density could be accommodated by either cell. The monoclinic cell was, however, appropriate for the bis compound, $Co(tu)_2Cl_2$ with $Z = 4$, $d_{\text{calcd}} = 1.85$ g/cm^3. Space group absences hkl: $h + k = 2n + 1$ and $h0l$: $l = 2n + 1$ indicated space groups Cc or C2/c. Intensities of 1432-nonzero reflections were collected on a GE XRD-5 manual diffractometer using Zr-filtered Mo radiation and a stationary crystal, stationary counter technique. A partial solution was achieved in the noncentrosymmetric space group Cc by standard Patterson and Fourier techniques. All of the nonhydrogen atoms were located and least-squares refinement proceeded with the Co, S, and Cl atoms treated anisotropically and the N and C atoms isotropically to a conventional R value of 0.14. The two carbon atoms refined to locations approximately 0.2 Å from the positions expected on the basis of the remainder of the structure owing to some disorder or other problems. We therefore report here only the positions of the cobalt and the four heavy atoms in the coordination sphere (Table II). Owing to the limited chemical interest of the present structure no further X-ray work or refinement is contemplated. A difference synthesis showed no evidence of a third thiourea molecule, confirming the fact that the crystal was indeed $Co(tu)_2Cl_2$. The expected somewhat distorted tetrahedral coordination is evident. The observed bond distances and angles (Table III) are unremarkable and compare well with those reported for $Zn(tu)_2Cl_2$.[4] It is interesting that these two similar substances are not isomorphous.

During the course of our X-ray work O'Connor and Amma[5] reported the structure of the tetragonal tetrakis complex, $Co(tu)_4Cl_2$, the cell dimensions of which are identical with those of the tetragonal crystals found in our sample of tris complex. It became apparent at this point that the tris complex was not a compound at all, but was in fact an *equimolar mixture of* $Co(tu)_2Cl_2$ *and* $Co(tu)_4Cl_2$. This was confirmed by a comparison of X-ray powder patterns obtained from

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TABLE I

ANALYTICAL AND MOLECULAR WEIGHT DATA[a]

Compound	% C Calcd	% C Found	% H Calcd	% H Found	% N Calcd	% N Found	% halogen Calcd	% halogen Found	% Co Calcd	% Co Found	Formula wt	Mol wt[b]	Mp, °C
$Co(CH_4N_2S)_2Cl_2$	8.52	8.57	2.86	2.85	19.87	19.96	...	...	...	...	282.07	287	145–146
$Co(CH_4N_2S)_2Br_2$	6.47	6.49	2.17	2.17	15.11	15.12	...	...	...	...	370.97	342	163.5
"$Co(CH_4N_2S)_3Cl_2$"	10.06	10.03	3.38	3.34	23.47	23.52	19.79	19.82	16.45	16.42	358.19	184	111
"$Co(CH_4N_2S)_3Cl_2$"[c]	10.06	10.15	3.38	3.26	23.47	23.27	19.79	20.08	16.45	16.28	358.19	178	111–115
"$Co(CH_4N_2S)_3Br_2$"	8.06	8.34	2.71	2.63	18.80	19.08	35.74	35.85	13.18	13.06	447.09	230	108–109
$Co(CH_4N_2S)_4Cl_2$	11.06	10.95	3.72	3.60	25.81	25.59	16.32	16.47	13.57	13.26	434.31	171	117–121

[a] Galbraith Laboratories, Knoxville, Tenn. [b] In acetone solution at 37° by osmometry. [c] Sample recrystallized from acetone.

TABLE II

FINAL ATOMIC POSITIONAL COORDINATES FOR THE CoS_2Cl_2 MOIETY IN $Co(tu)_2Cl_2$[a]

Atom	x	y	z
Co	0.0000[b]	0.1822 (3)	0.2500[b]
S(1)	0.1834 (9)	0.2253 (8)	0.1251 (7)
S(2)	−0.2104 (10)	0.0993 (6)	0.0933 (7)
Cl(1)	0.1149 (11)	0.0671 (6)	0.4180 (8)
Cl(2)	−0.1132 (9)	0.3356 (6)	0.3250 (8)

[a] Here and in Table III the standard deviations of the least significant figure(s) are given in parentheses. [b] Parameter specified arbitrarily to fix origin.

TABLE III

BOND DISTANCES AND ANGLES OF THE CoS_2Cl_2 MOIETY

Distances, Å			
Co–S(1)	2.30 (1)	Co–Cl(1)	2.29 (1)
Co–S(2)	2.32 (1)	Co–Cl (2)	2.27 (1)
Angles, Deg			
S(1)–Co–S(2)	97.6 (3)	S(1)–Co–Cl(2)	114.2 (3)
Cl(1)–Co–Cl(2)	108.3 (3)	S(2)–Co–Cl(1)	115.0 (3)
S(1)–Co–Cl(1)	113.6 (3)	S(2)–Co–Cl(2)	107.8 (3)

authentic samples of $Co(tu)_2Cl_2$ and $Co(tu)_4Cl_2$ (the latter was kindly supplied by Professor Amma) with that of our tris sample. The powder patterns of recrystallized and unrecrystallized samples of the tris complex are indistinguishable from one another and appear to be a superposition of the patterns of the bis and tetrakis compounds. Listed below are the d spacings obtained from films exposed using nickel-filtered copper radiation (λ 1.54178 Å for $K\bar{\alpha}$). The films suffer from considerable general blackening owing to fluorescence. The relative intensities are quoted on a common scale for films obtained with equal exposure times.

$d(Co(tu)_2Cl_2)$: 6.24 w, 5.78 w, 5.16 m, 4.58 w, 3.87 w, 3.46 w, 3.30 w, 3.10 w, 2.99 w, 2.86 w, 2.57 w Å. $d(Co(tu)_4Cl_2)$: 6.61 s, 4.48 w, 3.84 m, 3.00 m, 2.88 w, 2.70 m, 2.37 m, 2.23 w, 2.18 w, 2.05 w, 1.86 w, 1.83 w, 1.81 w, 1.68 w, 1.64 w, 1.61 w Å. d(tris sample): 6.68 s, 6.22 w, 5.21 m, 4.55 m, 3.88 m, 3.47 w, 3.28 w, 3.12 w, 3.02 m, 2.85 w, 2.72 m, 2.58 w, 2.40 m, 2.25 w, 2.20 w, 2.04 w, 1.87 w, 1.84 w, 1.82 w, 1.69 w, 1.65 w, 1.62 w Å.

There remained only to show that the results of the physical measurements are those expected for a mixed sample. We found that the tetrakis compound has an electronic spectrum in acetone solution identical on a molar basis with that of $Co(tu)_2Cl_2$, suggesting the dissociation: $Co(tu)_4Cl_2 \rightarrow Co(tu)_2Cl_2 + 2tu$. A similar observation was made by O'Connor and Amma.[5] The effective molecular weight of the tetrakis compound in acetone solution is approximately one-third that expected for monomeric $Co(tu)_4Cl_2$ (Table I), also consistent with the above postulated dissociation. Thus a tris sample containing 0.5 mol of $Co(tu)_2Cl_2$ and 0.5 mol of $Co(tu)_4Cl_2$ will produce upon dissociation 1 mol of $Co(tu)_2Cl_2$ and 1 mol of tu yielding a molecular weight consistent with our findings for the tris sample.

The solid-state electronic (mull) spectrum of $Co(tu)_4Cl_2$, while different from that of $Co(tu)_2Cl_2$, is weak and relatively featureless in the region in which it would not be obscured by the strong spectrum of $Co(tu)_2Cl_2$.

Dash and Rao[2] obtained $\mu_{eff} = 4.18$ BM for the tris chloride compounds. This value is less than that of either $Co(tu)_2Cl_2$ (4.45 BM[3]) or $Co(tu)_4Cl_2$ (4.90 BM[3]). We measured the susceptibility of a powdered sample of the tris chloride by the Gouy method and obtained, at 296°K, χ_M^{cor} 9274×10^{-6} cgsu which includes a molar diamagnetic correction of 184×10^{-6} cgsu, but no TIP correction. Our measurements yield $\mu_{eff} = 4.71$ BM, in good agreement with the root-mean-square value (4.68 BM) expected for an equimolar mixture of the bis and tetrakis compounds.

Finally, the present findings suggest that the structural interferences very recently presented[6,7] for compounds with the tris stoichiometry may require modification. Furthermore, our results emphasize that caution should be used when attributing stoichiometric analytical results to the formation of specific compounds.

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