Single-crystal Paramagnetic Susceptibilities of Dichlorobis(semicarbazide)copper(II) and Bis(3-azapentane-1,5-diamine)copper(II)

By **Malcolm Gerloch** * and **Irène Morgenstern-Badarau**, University Chemical Laboratories, Lensfield Road, Cambridge CB2 1EW

The single-crystal paramagnetic susceptibilities of the title complexes have been measured in the range 20—300 K. The results are interpreted within a model which presupposes no artificially high symmetry and in which the ligand field is parameterized by the angular-overlap model. Simultaneous fitting to the reported electronic spectra helps to define bonding parameters in the semicarbazide system and is essential in the diamine complex. The angular-overlap parameters confirm the essential tetragonality of these molecules with opposite senses of distortion. σ-Bonding parameters are quite well determined but not π. A large difference between σ-bonding values for the middle and terminal N atoms of the diamine seems necessary to fit the reported spectrum.

THE calculation of paramagnetic properties of unsymmetrical transition-metal complexes has recently been described.[1] The ligand field is represented by the angular-overlap model (a.o.m.) and our current applications [2] of this model have been directed equally towards the establishment of bonding parameters from magnetism as to the testing of the model's utility for a wide range of complexes. Studies [2] of some tetrahedral and five-coordinate nickel(II) systems and of some octahedral cobalt(II) molecules have been particularly clear with respect to π bonding while leaving estimates of σ bonding less sharp. This undoubtedly reflects the participation of the nominal t_{2g} d orbitals in the ground states. Results with rather different clarity might be expected with d^9 octahedral copper complexes in which the unpaired electron occupies the e_g set. With this in mind, as well as the viability of the model in systems with small magnetic anisotropies, varying little with temperature, we have investigated the magnetic properties of two nominally octahedral complexes of copper(II). Dichlorobis(semicarbazide)copper(II) may be classified as a tetragonally elongated octahedron, while bis(3-azapentane-1,5-diamine)copper(II) has been described [3] as tetragonally compressed. We compare these molecules from this point of view after independently studying

---

[1] M. Gerloch and R. F. McMeeking, *J.C.S. Dalton*, 1975, 2443.

[2] D. A. Cruse and M. Gerloch, *J.C.S. Dalton*, 1977, 1613 and refs. therein.

[3] B. J. Hathaway, M. J. Beur, and D. E. Billing, *J. Chem. Soc. A*), 1970, 1090.

their magnetic and spectral properties and, in addition, attempt to determine the π-bonding parameters for the oxygen and chlorine ligands in the semicarbazide complex. No π bonding is envisaged in the diamine complex.

EXPERIMENTAL

Dichlorobis(semicarbazide)copper(II).—Large blue crystals were grown from a mixture of excess of semicarbazide hydrochloride and $CuCl_2$ in water. Satisfactory C, N, and H analyses were obtained.

Magnetic susceptibilities were determined, using the Faraday balance and procedures recently described,[4] from crystals weighing *ca.* 6 and 8 mg, in the temperature range 20—300 K. The crystals are monoclinic. Two orientations were used. (*i*) // *b* from which values of the principal crystal susceptibilities χ_1 and χ_2 were measured directly. Observation of the orientation of χ_2 ($>\chi_1$ by definition [5]) with respect to the *a* and *c* crystal axes gave ϕ, the angle subtended by χ_1 and *a*, measured from *a* towards *c*, as $-42 \pm 5°$. (*ii*) // *c* gave values of $\chi_3 \equiv \chi_b$ and $\chi_{a'}$, the susceptibility in a direction perpendicular to both *b* and *c*. Values for $\chi_{a'}$ were determined at a few temperatures only to check on the value of ϕ which may be calculated from equation (1) in which β is the monoclinic angle. ϕ Values

$$\sin^2(\beta - 90 - \phi) = (\chi_{a'} - \chi_1)/(\chi_2 - \chi_1) \qquad (1)$$

calculated in this way ranged smoothly from −41° at 295 K to −30° at 35 K, confirming the estimate from the mounting // *b*. The temperature variation of ϕ may not be real, for results from (1) need not be very accurate, depending as they do on a ratio of differences between principal susceptibilities. In Table 1 are listed observed interpolated principal and average susceptibilities and mean moments throughout the temperature range.

TABLE 1

Observed principal crystal susceptibilities (χ/c.g.s. units × 10^{-6}), experimental calculated average susceptibilities, and moments (μ/B.M.) of dichlorobis(semicarbazide)-copper(II)

T/K	χ_1	χ_2	χ_3	$\bar{\chi}$	$\bar{\mu}$
295	1 280	1 580	1 290	1 380	1.80
285	1 320	1 630	1 330	1 430	1.80
275	1 370	1 690	1 380	1 480	1.80
265	1 420	1 750	1 430	1 530	1.80
255	1 470	1 820	1 480	1 590	1.80
245	1 530	1 890	1 540	1 650	1.80
235	1 590	1 960	1 610	1 720	1.80
225	1 660	2 040	1 680	1 800	1.80
215	1 740	2 140	1 760	1 880	1.80
205	1 830	2 250	1 840	1 970	1.80
195	1 930	2 370	1 940	2 080	1.80
185	2 040	2 500	2 050	2 200	1.80
175	2 150	2 640	2 160	2 320	1.80
165	2 280	2 790	2 280	2 450	1.80
155	2 420	2 950	2 420	2 600	1.79
145	2 580	3 150	2 570	2 770	1.79
135	2 770	3 380	2 760	2 970	1.79
125	2 990	3 650	2 980	3 260	1.79
115	3 240	3 950	3 230	3 470	1.79
105	3 540	4 290	3 520	3 780	1.78
95	3 930	4 750	3 910	4 200	1.79
85	4 420	5 350	4 410	4 730	1.79
75	5 040	6 110	5 000	5 390	1.80
65	5 810	7 070	5 730	6 200	1.80
55	6 920	8 430	6 820	7 390	1.80
45	8 350	10 180	8 280	8 940	1.79
35	10 820	13 190	10 780	11 600	1.80
25	15 160	18 620	15 140	16 310	1.81

Bis(3-azapentane-1,5-diamine)copper(II).—Large orthorhombic crystals were prepared by slow evaporation of a solution of excess of ligand and copper nitrate in water. Satisfactory C, N, and H analyses were obtained.

Susceptibility measurements were made, as before, on crystals weighing *ca.* 14 and 20 mg, based again on two orientations: (*i*) // *a*, giving χ_b and χ_c; and (*ii*) // *b*, giving χ_a and χ_c. Values for χ_c from the different orientations of two different crystals agreed to better than 1%. Results for χ_a, χ_b, and χ_c [the latter an average from (*i*) and (*ii*)] are listed in Table 2, together with calculated values of $\bar{\chi}$ and $\bar{\mu}$.

TABLE 2

Observed principal crystal susceptibilities (χ/c.g.s. units × 10^{-6}), experimental calculated average susceptibilities, and moments (μ/B.M.) of bis(3-azapentane-1,5-diamine)copper(II)

T/K	χ_a	χ_b	χ_c	$\bar{\chi}$	$\bar{\mu}$
295	1 310	1 320	1 360	1 330	1.77
285	1 360	1 360	1 400	1 380	1.77
275	1 420	1 420	1 460	1 440	1.78
265	1 480	1 480	1 520	1 490	1.78
255	1 530	1 540	1 580	1 550	1.78
245	1 590	1 600	1 650	1 610	1.78
235	1 650	1 660	1 720	1 680	1.77
225	1 720	1 740	1 790	1 750	1.77
215	1 800	1 810	1 880	1 830	1.77
205	1 900	1 900	1 970	1 920	1.78
195	1 990	2 010	2 080	2 030	1.78
185	2 100	2 120	2 190	2 140	1.78
175	2 210	2 230	2 310	2 250	1.78
165	2 350	2 360	2 440	2 380	1.77
155	2 490	2 520	2 580	2 530	1.77
145	2 650	2 710	2 740	2 700	1.77
135	2 840	2 910	2 930	2 890	1.77
125	3 060	3 140	3 160	3 120	1.77
115	3 330	3 410	3 440	3 390	1.77
105	3 640	3 730	3 750	3 720	1.76
95	4 030	4 140	4 160	4 110	1.77
85	4 490	4 640	4 650	4 590	1.77
75	5 090	5 280	5 280	5 210	1.77
65	5 850	6 070	6 070	6 000	1.77
55	6 930	7 210	7 230	7 130	1.77
45	8 330	8 700	8 760	8 600	1.76
35	10 790	11 260	11 310	11 120	1.76
25	15 130	15 790	15 850	15 590	1.77

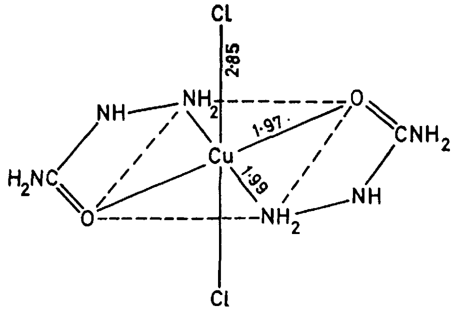

FIGURE 1 Co-ordination geometry of dichlorobis(semicarbazide)copper(II)

DISCUSSION

Dichlorobis(semicarbazide)copper(II).—The essential features of this centrosymmetric molecule [6] are shown in Figure 1. Calculations were made within the complete ^2D free-ion term as basis, perturbed by spin–orbit

---

[4] D. A. Cruse and M. Gerloch, *J.C.S. Dalton*, 1977, 152.

[5] M. Gerloch and P. N. Quested, *J. Chem. Soc.* (*A*), 1971, 2308.

[6] M. A. Hitchman, *J.C.S. Faraday II*, 1972, 846.

coupling and the ligand field. In addition to ζ, the spin–orbit coupling parameter, and k, Stevens' orbital-reduction factor, we have the following angular-overlap parameters: e_{σ}(Cl), e_{σ}(N), and e_{σ}(O) representing σ-bonding interactions between the copper atom and chlorine nitrogen- and oxygen-donor atoms, respectively; e_{π}(Cl) to describe π bonding from the chlorine atom which is presumed to be cylindrically symmetric with respect to the Cu–Cl bonds (*i.e.* a true 'spectroscopic' π bond); e_{π}(N) presumed negligible; and $e_{\pi\perp}$(O) and $e_{\pi//}$(O) representing π bonding from the oxygen atom in directions perpendicular and parallel to the Cu–O–C–NH moiety, respectively. We expect from the outset that $e_{\pi//}$(O) is zero, but we have not imposed this condition *a priori*.

Fitting calculated susceptibilities to those observed progressed in several stages. In order to limit the number of parameters being varied simultaneously we initially set e_{π}(Cl)/e_{σ}(Cl) and $e_{\pi\perp}$(O)/e_{σ}(O) at 0.25 in accordance with the results of an idealized calculation [6] based on overlap considerations. Two values for ζ, 500 and 700 cm^{-1}, were considered while e_{σ} for Cl, N, and O ranged independently from 4 000—8 000 cm^{-1}: $e_{\pi//}$(O) was set at zero. Best agreement with experiment, which was rather poor, was obtained for the higher value of ζ and lower values of e_{σ}(Cl). Somewhat higher values for e_{σ}(N,O) seemed appropriate, together with a clear indication of their approximate equality. Next, values for ζ, e_{σ}(Cl), and $e_{\sigma}(\mathrm{N}) = e_{\sigma}(\mathrm{O})$ were fixed at 700, 4 000, and 5 000 cm^{-1}, respectively, and the dependence of fits on e_{π} parameters were studied in the ranges 250—1 250 cm^{-1} for e_{π}(Cl) and $e_{\pi\perp}$(O), and 0—450 cm^{-1} for $e_{\pi//}$(O). From these calculations it was evident that e_{π}/e_{σ} values as high as 0.25 are quite inappropriate here. There were strong indications for low values, tending to zero, for all the three π-bonding parameters. Such a conclusion, arrived at by straightforward mechanical-fitting procedures, seems completely sensible for e_{π}(Cl) in view of the long Cu–Cl bond length of 2.85 Å: indeed, the indication so far of a smaller e_{σ}(Cl) value, compared with those for N and O, follows a similar pattern. A negligible value for $e_{\pi//}$(O) at this stage confirms initial expectations about the lack of any π bonding from O in the plane of the semicarbazide ligand. The possibility of there being a non-zero value for e_{π}(O) in this plane resulting from the model's inability to properly account for 'misdirected valency' (see refs. 1 and 4) is also discounted in view of the near identical geometries of the co-ordinated and free semicarbazide ligands.[7] Accordingly, in the next round of calculations e_{π}(Cl) and $e_{\pi//}$(O) were held at zero: with $\zeta = 700$ cm^{-1}, e_{σ}(O), held equal to e_{σ}(N), was varied from 3 000 to 7 000 cm^{-1} and e_{σ}(Cl) from 1 000 to 4 000 cm^{-1}; $e_{\pi\perp}$(O) ranged from -500 to $+1\,000$ cm^{-1}. A k value of 0.5—0.6 gave the best agreement with the observed susceptibilities, and was a fairly sensitive parameter. Little information was gained about $e_{\pi\perp}$(O), quite good agreement with experiment being possible for all the positive and negative values in the range studied. A value of 5 000 cm^{-1} was favoured for e_{σ}(N,O): agreement with observed magnetic properties falls off rapidly for $e_{\sigma}(\mathrm{N,O}) < 5\,000$ cm^{-1} but rather more slowly for values $>5\,000$ cm^{-1}. Fits were better for the lower values of e_{σ}(Cl) but the variation was small.

The dependence of fits on e_{σ}(Cl) and ζ was next investigated in more detail. With e_{σ}(N,O) fixed at 5 000 cm^{-1}, e_{σ}(Cl) in the range 2 000—5 000 cm^{-1}, and $e_{\pi\perp}$(O) $-1\,000$ to $+\,1\,000$ cm^{-1}, ζ was varied from 600 to 800 cm^{-1} in 100-cm^{-1} steps, for k 0.1—0.6. Best fits were confirmed for $k = 0.5$—0.6, there being some correlation with ζ values, the lower k linking with $\zeta = 800$ cm^{-1}, the higher with $\zeta = 700$ cm^{-1}. Fits, which were now good, were better for $e_{\sigma}(\mathrm{Cl}) = 4\,000$ than for 3 000 than for 2 000 cm^{-1}: however, agreement with $e_{\sigma}(\mathrm{Cl}) = 5\,000$ cm^{-1} was bad. The dependence of fits on $e_{\pi\perp}$(O) was still slight, negative values giving better agreement than positive ones but without significance.

The diffuse-reflectance spectrum [8] of this complex reveals bands at 14 600 and (as a shoulder) 13 000 cm^{-1}. The parameter values thus far determined from the magnetic work predict spectral transitions in fair agreement with these band maxima. There is some suggestion that spectral fits favour positive $e_{\pi\perp}$(O) values, but not much. Spectral fits appear better for larger ζ values but again not much. e_{σ}(N,O) values somewhat lower than 5 000 cm^{-1} are also favoured but little can be drawn from these calculations about e_{σ}(Cl). Variations of e_{σ}(Cl) in the range 2 000—4 000 cm^{-1} shift calculated spectral bands of energy $>5\,000$ cm^{-1} by less than 500 cm^{-1}: on the other hand, the calculated first excited state shifts from *ca.* 5 000 to *ca.* 1 700 cm^{-1} as e_{σ}(Cl) varies in this range. We recorded the single-crystal transmission spectrum at room temperature, down to 4 000 cm^{-1}. At $\leqslant 5\,000$ cm^{-1} we observed several i.r. bands characteristic of vibrational overtone structure, the appearance of which suggests no underlying electronic transition. Thus there is *probably* no electronic band in the 4 000—5 000 cm^{-1} region. This tentative negative evidence thus favours e_{σ}(Cl) values nearer 4 000 than 2 000 cm^{-1}.

Refinement of σ-bonding parameters by fitting to both susceptibility and spectral data was then performed, holding $e_{\pi\perp}$(O) constant at the (ill defined) value of $+500$ cm^{-1} and ζ at 800 cm^{-1}: e_{σ}(N,O) were varied from 4 500 to 5 500 cm^{-1} in 250-cm^{-1} steps and e_{σ}(Cl) from 3 000 to 4 000 cm^{-1} in 500-cm^{-1} steps, all independently. k ranged from 0.45 to 0.60 (in steps of 0.05). Fitting to susceptibilities strongly suggests almost equal values for e_{σ}(N) and e_{σ}(O) with a best-fit value of 4 500 cm^{-1}. A value of 5 000 cm^{-1} gives only slightly worse fits. Best fits were for $e_{\sigma}(\mathrm{Cl}) = 4\,000$ cm^{-1}, although 3 000 cm^{-1} was acceptable. k optimizes at 0.45. The spectrum adds little to those findings

---

[7] M. Nardelli, G. F. Gasparri, P. Boldrini, and G. G. Battistini, *Acta Cryst.*, 1965, **19**, 491.

[8] M. J. Campbell and R. Grzeskowiock, *J. Inorg. Nuclear Chem.*, 1968, **30**, 1865.

except for $e_\sigma(\mathrm{N,O})$ for which $e_\sigma(\mathrm{N}) = e_\sigma(\mathrm{O}) = 4\,750\ \mathrm{cm}^{-1}$ is best. The best-compromise parameter set to reproduce spectral and magnetic properties is therefore:

$$e_\sigma(\mathrm{O}) = e_\sigma(\mathrm{N}) = 4\,750\ \mathrm{cm}^{-1},\ e_\sigma(\mathrm{Cl}) \leqslant 4\,000\ \mathrm{cm}^{-1}$$
$$e_\pi(\mathrm{Cl}) \sim 0,\ e_{\pi/\!/}(\mathrm{O}) \sim 0,\ e_{\pi\perp}(\mathrm{O}) < 1\,000\ \mathrm{cm}^{-1}\ \text{(probably positive)},\ \zeta = 800\ \mathrm{cm}^{-1},\ k = 0.45$$

The final comparison between the observed and calculated spectra (cm^{-1}) is as follows:

Observed	Calculated
14 600	14 520
	14 020
13 000	12 755
	1 240

The agreement between each calculated and observed crystal susceptibility is better than 3% throughout the temperature range, and we note here that the calculated ϕ value is $-36°$, which agrees well with the observed value of $-42 \pm 5°$. The corresponding calculated principal *molecular* susceptibilities describe the temperature-independent effective magnetic moments $\mu_1 = 1.76$, $\mu_2 = 1.77$, and $\mu_3 = 1.91$ B.M.* The direction cosines of the molecular-susceptibility ellipsoid with respect to the orthogonalized crystal frame are:

	a	b	c'
$\mu_1 = 1.76, K_1$	-0.091	0.060	0.050
$\mu_2 = 1.77, K_2$	0.029	0.084	-0.078
$\mu_3 = 1.91, K_3$	-0.096	-0.031	-0.116

From those values we calculate the orientations (°) of the principal molecular susceptibilities with respect to the major bond directions as follows:

	K_1	K_2	K_3
Cu–Cl	88.9	86.8	3.4
Cu–O	18.9	71.2	87.2
Cu–N	64.3	25.8	89.0

These directions vary by less than 3° throughout the temperature range. We note that the molecular magnetic ellipsoid is approximately axial with $K_{/\!/} > K_\perp$ so that the 'unique' susceptibility lies approximately parallel to the Cl–Cu–Cl molecular direction. In view of the major difference between ligand parameters being $e_\sigma(\mathrm{Cl}) < e_\sigma(\mathrm{N}) = e_\sigma(\mathrm{O})$, $e_{\pi\perp}(\mathrm{O})$ having rather little effect on moments, this result is unexceptional. That K_1 and K_2 are not oriented exactly towards the O or N donor atoms is of little significance in view of (*a*) the N–Cu–O chelate angle being <90° (actually 83°), (*b*) the non-zero $e_{\pi\perp}(\mathrm{O})$ value, and (*c*) the inevitable mixing between $d_{x^2-y^2}$ and d_{xy} orbitals caused by spin–orbit coupling.

Bis(3-*azapentane*-1,5-*diamine*)*copper*(II).—The molecular geometry [9] of this molecule, shown in Figure 2, has been described [3] as representative of a tetragonally compressed octahedron by virtue of the two short Cu–N bond lengths and four longer bonds to the terminal nitrogens. Calculations, again based on the complete ^2D term basis, were made using the following parameter set: $e_\sigma(\mathrm{N_T})$ and $e_\sigma(\mathrm{N_M})$ for σ bonding with terminal and middle nitrogen atoms, ζ for spin–orbit coupling, and k; π bonding has been presumed negligible. Fitting began by assuming that e_σ values were equal for the different nitrogens, calculations being made for $e_\sigma = 3\,000$—$7\,000\ \mathrm{cm}^{-1}$ in 500-cm^{-1} steps, and $\zeta = 400$—850 in 50-cm^{-1} steps. As usual, k ranged from 0.1 to 1.0. It was immediately apparent that little information could be obtained from a comparison of the susceptibility results alone. Although k is determined as *ca.* 0.5, the slight temperature dependence of the observed magnetic moments and especially the small anisotropies shown by these crystals make fitting to the other parameters completely insensitive. The observed sequence $\chi_c > \chi_b > \chi_a$ *is* reproduced by the calculations and quantitative agreement between observed and calculated χ values is acceptable.

Crystal-transmission spectra have been reported [3] for this complex with bands at 15 600, 11 700, and 9 200 cm^{-1} although the last two are barely resolved even at liquid-nitrogen temperatures. Calculations of the above type are quite incapable of reproducing these band energies. For example, with $e_\sigma = 5\,500\ \mathrm{cm}^{-1}$ band energies occur at *ca.* 15 800, 14 200, and 600 cm^{-1}. The maximum splitting of the higher-energy bands for 'isotropic' e_σ values is *ca.* 1 200 cm^{-1}. Accordingly, we reduced the restraint on e_σ values, considering ranges of 3 000—7 000 cm^{-1} (in 1 000-cm^{-1} steps) independently, with ζ values of 400 and 500 cm^{-1}. Comparison of the susceptibility values again suggests $k < 0.5$ with $\zeta = 450$ better than 500 cm^{-1}. Best fits actually occur with $e_\sigma(\mathrm{N_T}) = e_\sigma(\mathrm{N_M})$, but secondary and acceptable fits do occur for $e_\sigma(\mathrm{N_T}) < e_\sigma(\mathrm{N_M})$. Those with $e_\sigma(\mathrm{N_T}) > e_\sigma(\mathrm{N_M})$ are markedly worse. No *quantitative* assessment seems possible from the magnetism alone. Further, within these possible e_σ ranges, it is not possible to calculate transition energies simultaneously at *ca.* 15 600 and *ca.* 10 000 cm^{-1}. We found, however, that these bands *are* predicted for a markedly larger difference between bonding parameters for the two types of nitrogen atom. We also note that this is only possible for a relatively small range of e_σ values. Bands at 15 800, 15 600, 15 000, and 10 200 cm^{-1} are calculated with the parameter set $e_\sigma(\mathrm{N_M}) = 7\,000\ \mathrm{cm}^{-1}$, $e_\sigma(\mathrm{N_T}) = 2\,000\ \mathrm{cm}^{-1}$, and $\zeta = 400\ \mathrm{cm}^{-1}$. If one doubts the extent of this difference between e_σ values, we find only small variations are possible for spectral fits. For example, with

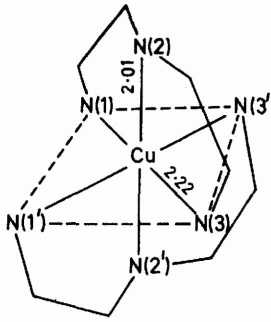

FIGURE 2 Co-ordination geometry of bis(3-azapentane-1,5-diamine)copper(II)

---

* Throughout this paper: 1 B.M. ≈ $9.27 \times 10^{-24}\ \mathrm{A\ m^2}$.

[9] F. S. Stephens, *J. Chem. Soc.* (*A*), 1969, 883.

$e_\sigma(\mathrm{N_M}) = 6\,500\ \mathrm{cm^{-1}}$, $e_\sigma(\mathrm{N_T}) = 2\,500\ \mathrm{cm^{-1}}$, and $\zeta = 700\ \mathrm{cm^{-1}}$ we calculate bands at 15 500, 15 100, 14 100, and 8 200 cm^{-1}. Thus a decrease in $[e_\sigma(\mathrm{N_M}) - e_\sigma(\mathrm{N_T})]$ rapidly forces down the energy of the first excited state. No selection of the parameter values yields bands at 15 600, 11 700, *and* 9 200 cm^{-1} as reported.

We are left in the position, therefore, of doubting the utility of the present model (but seen against its successes in the interpretation of many other systems) or that the barely resolved bands at 11 700 and 9 200 cm^{-1} actually reveal two distinct electronic transitions. Even then, the very small value of e_σ for the terminal nitrogen atoms required to reproduce a single transition at *ca.* 10 000 cm^{-1} does seem surprising. At least the relative magnitudes of $e_\sigma(\mathrm{N_T})$ and $e_\sigma(\mathrm{N_M})$ appear to correlate quantitatively with their relative bond lengths. Agreement between each calculated and observed crystal susceptibility throughout the complete temperature range is a little better than 2% for the parameter set:

$$e_\sigma(\mathrm{N_T}) = 6\,800\ \mathrm{cm^{-1}},\ e_\sigma(\mathrm{N_M}) = 2\,000\ \mathrm{cm^{-1}}$$
$$\zeta = 600\ \mathrm{cm^{-1}},\qquad k = 0.3$$

Thus band energies are calculated at 15 580, 15 320, 14 420, and 9 740 cm^{-1}. The corresponding *molecular* susceptibilities describe effective molecular magnetic moments $\mu_1 = 1.73$, $\mu_2 = 1.79$, and $\mu_3 = 1.79$ B.M. (which do not vary with temperature) and from which we note a near-perfect axiality of the molecular magnetic ellipsoid. The orientation (°) of the molecular property with respect to the crystal axes varies by less than 0.5° throughout the temperature range and is:

	a	*b*	*c*
$\mu_1 = 1.73, K_1$	134.5	122.6	62.0
$\mu_2 = 1.79, K_2$	135.5	60.3	119.8
$\mu_3 = 1.79, K_3$	92.0	47.0	43.1

With respect to the co-ordination bond directions the orientations are as follows:

	K_1	K_2	K_3
Cu–N$_\mathrm{M}$	11.8	79.6	87.2
Cu–N(1)	67.6	38.9	40.6
Cu–N(3)	86.4	36.4	49.3

Thus, the magnetic properties of this molecule are well described as axial with $K_{//} < K_\perp$ where $K_{//}$ lies close to the N$_\mathrm{M}$–Cu–N$_\mathrm{M}$ direction, so confirming the description of this geometry as that of a tetragonally compressed octahedron.

Conclusions.—All the calculations reported have made explicit recognition of the exact geometries of the co-ordination shells as defined by the reported structural analyses.[1] The processes of fitting these calculations to the observed susceptibilities and spectra have been described in full in order to show the independent, indeed mechanical, procedures employed which owe little to prejudice based on chemical or pseudo-symmetry considerations. Nevertheless, good fits to all the data have been obtained with bonding parameters which have chemically sensible values. A negligible degree of π bonding for the chlorine ligand in the semicarbazide complex is a reasonable result in view of the long Cu–Cl bond length, as is the lower e_σ bonding parameter for this ligand. The larger e_σ value for the shorter Cu–N bonds in the diamine complex compared with the terminal nitrogens is quantitatively sensible, although the magnitude of this difference, $e_\sigma \sim 6\,800$ and $2\,000\ \mathrm{cm^{-1}}$ for Cu–N bond lengths of 2.01 and 2.22 Å, respectively, deserves further study in other complexes. The values for e_σ(Cl) in the semicarbazide molecule might be compared with that in the tetrahedral ion $[\mathrm{CuCl_4}]^{2-}$. In the semicarbazide complex the Cu–Cl bond length is 2.84 Å and $e_\sigma \leqslant 4\,000\ \mathrm{cm^{-1}}$, while in $[\mathrm{CuCl_4}]^{2-}$ the Cu–Cl distance is 2.20 Å and $e_\sigma = 6\,800\ \mathrm{cm^{-1}}$, again a sensible result. A rough-and-ready estimate of Δ_oct in the semicarbazide, using the 'octahedral' relation (2) gives

$$\Delta_\mathrm{oct} = 3e_\sigma - 4e_\pi \qquad (2)$$

Δ_oct for a CuCl$_6$ moiety as *ca.* 13 000 cm^{-1}. Four ninths of this value is *ca.* 5 800 cm^{-1} which may be compared with Δ_tet in $[\mathrm{CuCl_4}]^{2-}$ (*ca.* 5 850 cm^{-1}). Thus, despite the considerable difference in Cu–Cl bond lengths in the two complexes, the geometry-based four ninths rule appears to work. The discrepancy is made up, of course, in the small (possibly negligible) degree of π bonding in the semicarbazide molecule compared with the value[10] (1 800 cm^{-1}) for e_π in $[\mathrm{CuCl_4}]^{2-}$.

It is disappointing that estimates of π bonding in the semicarbazide system have been semiquantitative at best. But this is hardly surprising in view of the dominance of the ground states in octahedral d^9 systems by a single hole in the e_g, *i.e.* σ-bonding, orbital. It is clear too that fitting to magnetic susceptibilities in these copper complexes can be insensitive because of the relatively small anisotropies and particularly because of the small temperature dependences of the principal susceptibilities. It is interesting to note the somewhat smaller anisotropy calculated for the molecules of the diamine complex compared with the semicarbazide system: the anisotropy in the *crystals* of the diamine complex is even smaller as a result of the unfortunate relative orientations of the symmetry-related molecules in the lattice.

Finally, we note that the calculated molecular susceptibilities closely describe tetragonally distorted octahedra in both molecules, but in opposite senses. In the semicarbazide molecule we have an elongation and $K_{//} > K_\perp$, while in the diamine system we have compression with $K_{//} < K_\perp$.

We thank Drs. J. E. Davies and D. J. Phillips and Mr. D. A. Cruse for help and advice, and the Royal Society and C.N.R.S. for support (to I. M.-B.).

[6/1998 *Received, 27th October,* 1976]

---

[10] D. A. Cruse and M. Gerloch, *J.C.S. Dalton*, preceding paper.