

Table III. Final Fractional Atomic Coordinates ( $\times 10^4$ )

atom	x/a	y/b	z/c
Rh(1)	2775 (1)	1029 (1)	3062 (1)
Rh(2)	1788 (1)	-947 (1)	1737 (1)
O(11)	4658 (10)	1292 (9)	3262 (6)
O(12)	4377 (12)	2670 (9)	4209 (6)
O(13)	6275 (13)	2757 (13)	4300 (8)
N(10)	5181 (15)	2296 (12)	3967 (9)
N(20)	3001 (17)	-2208 (13)	1041 (9)
O(22)	1877 (12)	-2673 (10)	673 (7)
O(23)	3754 (14)	-2625 (13)	837 (8)
O(21)	3426 (10)	-1193 (9)	1721 (6)
N(101)	3145 (12)	1899 (10)	2246 (7)
C(100)	2909 (15)	1257 (13)	1385 (9)
N(102)	2410 (13)	26 (11)	1014 (7)
C(111)	4284 (15)	4140 (14)	3154 (9)
C(112)	4263 (16)	5278 (15)	3451 (10)
C(113)	3290 (16)	5424 (15)	3119 (10)
C(114)	2304 (16)	4405 (15)	2441 (10)
C(115)	2318 (16)	3266 (15)	2162 (10)
C(110)	3247 (15)	3132 (13)	2511 (9)
C(116)	3273 (17)	6657 (15)	3483 (12)
C(121)	1323 (14)	-1335 (13)	-495 (9)
C(122)	1283 (14)	-1808 (13)	-1375 (9)
C(123)	2367 (15)	-1344 (14)	-1660 (10)
C(124)	3495 (14)	-391 (13)	-1039 (9)
C(125)	3527 (14)	28 (13)	-176 (9)
C(120)	2408 (14)	-450 (13)	123 (9)
C(126)	2380 (20)	-1833 (17)	-2625 (10)
N(201)	2392 (12)	11 (11)	3790 (7)
C(200)	1667 (15)	-1211 (12)	3374 (9)
N(202)	1246 (12)	-1818 (10)	2548 (7)
C(211)	2645 (14)	1422 (13)	5270 (9)
C(212)	2990 (16)	1754 (15)	6153 (10)
C(213)	3593 (15)	1237 (15)	6488 (10)
C(214)	3850 (15)	343 (14)	5939 (10)
C(215)	3479 (14)	-15 (14)	5039 (9)
C(210)	2847 (14)	472 (13)	4698 (9)
C(216)	3965 (20)	1659 (18)	7469 (10)
C(221)	181 (15)	-4110 (14)	1684 (10)
C(222)	-967 (17)	-5224 (16)	1428 (11)
C(223)	-2021 (15)	-5280 (14)	1689 (10)
C(224)	-2028 (17)	-4237 (16)	2264 (11)
C(225)	-920 (16)	-3106 (15)	2539 (10)
C(220)	152 (14)	-3017 (13)	2268 (9)
C(226)	-3246 (20)	-6520 (16)	1381 (13)
N(301)	1030 (13)	900 (11)	2981 (7)
C(300)	61 (15)	44 (13)	2344 (9)
N(302)	196 (14)	-831 (11)	1680 (8)
C(311)	1717 (15)	2976 (14)	4104 (10)
C(312)	1515 (15)	3808 (13)	4811 (9)
C(313)	407 (15)	3431 (14)	5097 (10)
C(314)	-493 (17)	2217 (16)	4697 (11)
C(315)	-253 (15)	1386 (14)	4020 (10)
C(310)	837 (14)	1749 (13)	3708 (9)
C(316)	186 (21)	4345 (18)	5831 (11)
C(321)	-1014 (15)	-2912 (14)	549 (10)
C(322)	-2158 (15)	-3861 (14)	-69 (10)
C(323)	-3220 (14)	-3744 (13)	-240 (9)
C(324)	-3117 (15)	-2565 (14)	231 (10)
C(325)	-1999 (13)	-1582 (12)	853 (8)
C(320)	-940 (14)	-1747 (12)	1032 (9)
C(326)	-4404 (16)	-4769 (14)	-918 (10)

Figure 1 illustrates the molecular structure of the complex  $\text{Rh}_2(\text{Form})_3(\text{NO}_3)_2$  and atomic labeling scheme. Selected bond distances and angles are shown in Table I; some relevant torsional angles and the final fractional atomic coordinates are given in Tables II and III, respectively.

The molecular structure consists of three formamidinate bridging ligands symmetrically disposed about the Rh-Rh unit with the two bidentate nitrate groups unsymmetrically coordinated to each rhodium atom. The Rh-Rh bond distance of 2.485 (1) Å is quite long if compared with the distances found in the complex  $[\text{Rh}_2(\text{O}_2\text{CCH}_2)_4(\text{H}_2\text{O})_2]^{+2a}$  and most of the  $\text{Rh}_2^{4+}$  derivatives,<sup>1</sup> especially if we consider that the increased positive charge on the rhodium atoms of  $\text{Rh}_2(\text{Form})_3(\text{NO}_3)_2$  ought to increase the order bond. But the Rh-Rh separation in such complexes is dependent

on the nature and the number of the bridging ligands. The reduced number and the different constraining effect of the bridging ligands can explain the longer Rh-Rh distance in the title complex.

The equatorial Rh(1)-O(11) and Rh(2)-O(21) bond lengths, respectively 2.090 (13) and 2.086 (13) Å, are significantly shorter than the axial Rh(1)-O(12) = 2.287 (8) Å and Rh(2)-O(22) = 2.382 (12) Å, in accordance with the high trans influence of the Rh-Rh bond. The very small O(11)-Rh(1)-O(12) = 57.3 (4)° and O(21)-Rh(2)-O(22) = 56.3 (5)° bond angles and the values of 95.6 (3) and 99.0 (3)° for the angles Rh(1)-Rh(2)-O(21) and Rh(2)-Rh(1)-O(11) are clearly imposed by the bidentate coordination of the nitrate groups which are then responsible for the distortion from the normal octahedral coordination around each rhodium atom.

Each rhodium atom completes its coordination with three nitrogen atoms of the bridging ligands. The two formamidinate groups in transoid positions exhibit a mean Rh-N distance of 2.033 Å while the Rh-N distances of the third bridging ligand are significantly shorter (Rh(2)-N(302) = 1.946 (18) Å, Rh(1)-N-(301) = 1.985 (16) Å). All the five-membered rings Rh-Rh-N-C-N deviate from the planarity and are twisted by an average of 6.35° (see Table II) from the eclipsed conformation. The ring C-N distances show considerable double-bond character, indicating that extensive delocalization occurs within the fragment N-C-N.

The symmetrical mixed-valence complex  $\text{Rh}_2(\text{Form})_3(\text{NO}_3)_2$  lies within the Robin and Day class II or III-A compounds,<sup>12</sup> and spectroscopic evidence is necessary to determine whether the oxidation states are integral (class II) or not (class III-A). However, we suspect, on the basis of the X-ray structural data, which show the symmetrical arrangement of the five anionic ligands around each rhodium atom, that in the title complex the rhodium sites are equivalent. This implies that it is not possible to locate the unpaired electron on one of the two rhodium atoms and that the formal oxidation state for each rhodium atom is 2.5.

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**Registry No.**  $\text{Rh}_2(\text{Form})_3(\text{NO}_3)_2$ , 99416-57-6;  $[\text{Rh}(\text{C}_8\text{H}_{12})(\text{Form})]_2$ , 81229-43-8; Rh, 7440-16-6.

**Supplementary Material Available:** Listings of interatomic distances and angles associated with the tolyl fragments and nitrate groups (Table IV), hydrogen atom parameters (Table V), temperature factors (Table VI), and structure factors (22 pages). Ordering information is given on any current masthead page.

(12) Robin, M. B.; Day, P. *Adv. Inorg. Chem. Radiochem.* 1967, 10, 247.

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### Interpretation of Copper(II) Hyperfine Parameters

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The effects of hyperfine coupling in EPR spectroscopy were first observed during the study of a copper(II) complex,<sup>1</sup> and these data provided the impetus for the derivation of the basic ex-

(1) Penrose, R. P. *Nature (London)* 1949, 163, 992.

Table I. Calculated and Observed Metal Hyperfine Parameters

complex <sup>a</sup>	geometry <sup>b</sup>	g shifts			excited state <i>E</i> , cm <sup>-1</sup> × 10 <sup>3</sup>		metal hyperfine parameters, cm <sup>-1</sup> × 10 <sup>4</sup>					
							calcd				obsd	
							using g shifts		using coeff			
$\Delta g_z$	$\Delta g_{xy}$	$\alpha^2$ <sup>c</sup>	<i>E</i> <sub>xy</sub>	<i>E</i> <sub>xz,yz</sub>	<i>A</i> <sub>z</sub>	<i>A</i> <sub>xy</sub>	<i>A</i> <sub>z</sub>	<i>A</i> <sub>xy</sub>	<i>A</i> <sub>z</sub>	<i>A</i> <sub>xy</sub>		
Cu(NH <sub>3</sub> ) <sub>4</sub> <sup>2+</sup> <sup>d</sup>	planar	0.197	0.036	0.78	20.7	20.7	-205	-30	-181	-23	212	45
CuCl <sub>4</sub> <sup>2-</sup> <sup>e</sup>	planar	0.230	0.047	0.73	12.5	14.25	-173	-25	-131	-17	164	35
Cu(acac) <sub>2</sub> <sup>f</sup>	planar	0.264	0.052	0.76	16.3	18.0	-171	-25	-167	-22	160	20
Cu(NO <sub>2</sub> ) <sub>6</sub> <sup>4-g</sup>	elong oct	0.275	0.075	0.78	16.0	16.0	-171	-19	-167	-20	160	19
Cu(H <sub>2</sub> O) <sub>6</sub> <sup>2+h</sup>	elong oct	0.463	0.097	0.78	10.0	12.0	-99	-13	-101	-13	112	16
Cu(1,10-phen)Cl <sub>2</sub> <sup>8</sup>	ps tet	0.295	0.060	0.71	13.0	11.63	-140	-20	-131	-12	123	9
Cu(Ph <sub>3</sub> PO) <sub>2</sub> Cl <sub>2</sub> <sup>11</sup>	ps tet	0.428	0.083	0.75	8.5	6.95	-103	-15	-62	5	40	25
Cs <sub>2</sub> Zn[Cu]Cl <sub>4</sub> <sup>6,7</sup>	ps tet	0.435	0.077	0.75	7.2	4.495	-102	-17	-16	29	25	48.5
(enH <sub>2</sub> C1) <sub>2</sub> Zn[Cu]Cl <sub>4</sub> <sup>6</sup>	ps tet	0.433	0.005	0.75	7.8	5.36	-87	-48	-23	60	2	71
			0.208			4.42		17		9		43
CuF <sub>6</sub> <sup>4-20</sup>	compr oct	0.002	0.397	0.77	10.8	8.2	19	-45	18	-39	78	30

<sup>a</sup>References to the EPR parameters and excited state energies are given below. Key: acac = acetylacetonate anion, 1,10-phen = 1,10-phenanthroline, Ph<sub>3</sub>PO = triphenylphosphine oxide, enH<sub>2</sub>C1 = 1,2-diaminoethane hydrochloride. <sup>b</sup>Key: elong oct = elongated octahedral, ps tet = pseudotetrahedral, compr oct = compressed octahedral. <sup>c</sup>Unpaired spin density in the metal part of the ground state, estimated in most cases as  $1 - \alpha^2$  where  $\alpha^2$  is the unpaired spin density on the ligands deduced from ligand superhyperfine structure. <sup>d</sup>Schneider, W.; Baccini, P. *Helv. Chim. Acta* **1969**, *52*, 1955. <sup>e</sup>Chee, Chow; Kun, Chang; Willett, R. D. *J. Chem. Phys.* **1973**, *59*, 2629. Hitchman, M. A.; Cassidy, P. *Inorg. Chem.* **1978**, *17*, 1682. <sup>f</sup>Maki, A. H.; McGarvey, B. R. *J. Chem. Phys.* **1958**, *29*, 31. Getz, D.; Silver, B. L. *Inorg. Chem.* **1976**, *15*, 1240. Ferguson, J. J. *Chem. Phys.* **1961**, *34*, 1609. <sup>g</sup>Joesten, M. D.; Venable, J. H., Jr. *Inorg. Chem.* **1983**, *22*, 1733. Reinen, D.; Friebel, C. *Struct. Bonding (Berlin)* **1979**, *37*, 1. <sup>h</sup>Breen, D. P.; Krupka, D. C.; Williams, F. I. B. *Phys. Rev.* **1969**, *179*, 241. Getz, D.; Silver, B. L. *J. Chem. Phys.* **1974**, *61*, 630. Hitchman, M. A.; Waite, T. D. *Inorg. Chem.* **1976**, *15*, 2150.

pressions used to interpret the hyperfine parameters of axially symmetric copper(II) compounds given in the following equations:<sup>2</sup>

for a  $d_{x^2-y^2}$  or  $d_{xy}$  ground state

$$A_z = P(-K\alpha^2 - \frac{4}{7}\alpha^2 + \frac{6}{7}C_2 + 8C_1) \quad (1a)$$

$$A_{xy} = P(-K\alpha^2 + \frac{2}{7}\alpha^2 + \frac{1}{7}C_2) \quad (1b)$$

for a  $d_{z^2}$  ground state

$$A_z = P(-K\alpha^2 + \frac{4}{7}\alpha^2 - \frac{6}{7}C_2) \quad (1c)$$

$$A_{xy} = P(-K\alpha^2 - \frac{2}{7}\alpha^2 + \frac{4}{7}C_2) \quad (1d)$$

Here,  $K$  represents an isotropic component due to unpaired spin density in the metal  $s$  orbitals, the factors  $\pm 4/7$  and  $\pm 2/7$  represent the dipolar contributions from unpaired spin in the highest energy  $d$  orbital, and the coefficients  $C_1$  and  $C_2$  take into account contributions from the lower energy  $d_{xy}$  (or  $d_{x^2-y^2}$ , if the ground state is  $d_{xy}$ ) and  $d_{xz,yz}$  orbitals mixed into the ground state by spin-orbit coupling. The parameter  $P = g_e g_N \beta_e \beta_N \langle r^{-3} \rangle$ , which has been estimated as  $\sim 360 \times 10^{-4} \text{ cm}^{-1}$  for copper(II) compounds,<sup>3</sup> is essentially a scaling factor representing the average distance of a  $d$  electron from the nucleus, while the coefficient  $\alpha^2$  represents the spin density in the highest energy  $d$  orbital, that transferred to ligands being assumed to make a negligible contribution to the metal hyperfine coupling because of the steep way in which this decreases with increasing electron-nuclear distance. Polarization of core  $s$  electrons has been estimated to produce a value of  $K = 0.43$  for copper(II),<sup>4</sup> though when allowed by symmetry a negative contribution to  $K$  due to direct occupancy of the metal  $4s$  orbital may occur.<sup>3</sup>

The assumption of a conventional molecular orbital description of the bonding in a metal complex implies the relationships between the coefficients  $C_1$  and  $C_2$  and the excited states  $E_{xy}$  (or

$E_{x^2-y^2}$ ) and  $E_{xz,yz}$  shown in eq 2.<sup>5</sup> Here,  $\alpha$ ,  $\beta$ , and  $\gamma$  are the

$$C_1 = \frac{-\alpha^2 \beta^2 \lambda}{E_{xy}} \quad C_2 = \frac{-\alpha^2 \gamma^2 \lambda}{E_{xz,yz}} \quad (2)$$

coefficients of  $d_{x^2-y^2}$ ,  $d_{xy}$ , and  $d_{xz,yz}$  in the appropriate molecular orbital and  $\lambda = -828 \text{ cm}^{-1}$  is the spin-orbit coupling constant of copper(II). Presumably because the values of  $E_{xy}$ , etc., and  $\alpha^2$ , etc., are not always known it has become the practice to use the molecular  $g$  shifts from the free electron value to estimate  $C_1$  and  $C_2$  via the following relationships:

for a  $d_{x^2-y^2}$  (or  $d_{xy}$ ) ground state

$$\Delta g_z = \frac{-8k_x^2 \lambda}{E_{xy} \text{ (or } E_{x^2-y^2})} \quad \Delta g_{xy} = \frac{-2k_{xy}^2 \lambda}{E_{xz,yz}} \quad (3a)$$

for a  $d_{z^2}$  ground state

$$\Delta g_{xy} = \frac{-6k_{xy}^2 \lambda}{E_{xz,yz}} \quad (3b)$$

Here  $k_{xy}$  and  $k_z$  are the so-called orbital reduction parameters, and it should be noted that it is implicit in the assumption that eq 2 and 3 may be combined to yield estimates of  $C_1$  and  $C_2$  that  $k_z^2 \approx \alpha^2 \beta^2$  and  $k_{xy}^2 \approx \alpha^2 \gamma^2$ . The expressions obtained in this way, conventionally used to interpret metal hyperfine parameters,<sup>5</sup> are shown in the following equations:

for a  $d_{x^2-y^2}$  (or  $d_{xy}$ ) ground state

$$A_z = P(-K\alpha^2 - \frac{4}{7}\alpha^2 + \frac{3}{7}\Delta g_{xy} + \Delta g_z) \quad (4a)$$

$$A_{xy} = P(-K\alpha^2 + \frac{2}{7}\alpha^2 + \frac{1}{14}\Delta g_{xy}) \quad (4b)$$

for a  $d_{z^2}$  ground state

$$A_z = P(-K\alpha^2 + \frac{4}{7}\alpha^2 - \frac{1}{7}\Delta g_{xy}) \quad (4c)$$

$$A_{xy} = P(-K\alpha^2 - \frac{2}{7}\alpha^2 + \frac{4}{42}\Delta g_{xy}) \quad (4d)$$

## Discussion

While eq 4a and 4b have been successfully used to interpret

- (2) Abragam, A. *Phys. Rev.* **1950**, *79*, 534. Abragam, A.; Pryce, M. H. L. *Proc. R. Soc. London, Ser. A* **1951**, *206*, 164. Abragam, A.; Bleaney, B. "Electron Paramagnetic Resonance of Transition Ions"; Clarendon Press: Oxford, England **1970**; p 456.  
 (3) McGarvey, B. R. *J. Phys. Chem.* **1967**, *71*, 51.  
 (4) Abragam, A.; Pryce, M. H. L. *Proc. Roy. Soc. London, Ser. A* **1955**, *230*, 169.  
 (5) McGarvey, B. R. *Transition Met. Chem. (N.Y.)* **1966**, *3*, 89.

the hyperfine parameters observed for a wide range of planar and six-coordinate elongated tetragonal copper(II) complexes, they have proved inadequate for several pseudotetrahedral copper(II) compounds, in particular the  $\text{CuCl}_4^{2-}$  ion. This may be seen from the data in Table I, where  $A_z$  and  $A_{xy}$  calculated by using the observed  $g$  shifts and accepted values of  $P$  and  $K$  are compared with experimental data for a range of copper(II) complexes. In particular, the magnitude of  $A_z$  estimated for pseudotetrahedral  $\text{CuCl}_4^{2-}$  is far too large. The data recently reported<sup>6</sup> for  $(\text{enH}_2\text{Cl})_2\text{Zn}[\text{Cu}]\text{Cl}_4$ , en = 1,2-diaminoethane, are especially relevant, as in this system  $A_z \approx 0$ . Here, a significant rhombic component is present in the  $g$  and  $A$  tensors, necessitating the use of eq 5 in the interpretation of the hyperfine parameters. The

$$A_x = P(-K\alpha^2 + 2a^2(a^2 - b^2)/7 + 4(3^{1/2})\alpha^2 ab/7 + \Delta g_x - (3a - 3^{1/2}b)\Delta g_y/14(a + 3^{1/2}b) - \Delta g_z b/7a) \quad (5a)$$

$$A_y = P(-K\alpha^2 + 2a^2(a^2 - b^2)/7 - 4(3^{1/2})\alpha^2 ab/7 + \Delta g_y - (3a + 3^{1/2}b)\Delta g_x/14(a - 3^{1/2}b) + \Delta g_z b/7a) \quad (5b)$$

$$A_z = P(-K\alpha^2 - 4a^2(a^2 - b^2)/7 + (3a - 3^{1/2}b)\Delta g_y/14(a + 3^{1/2}b) + (3a + 3^{1/2}b)\Delta g_x/14(a - 3^{1/2}b) + \Delta g_z) \quad (5c)$$

coefficients  $a$  and  $b$ , estimated as  $\sim 0.96$  and  $\sim 0.27$ , respectively,<sup>6</sup> represent the relative contributions of  $d_{x^2-y^2}$  and  $d_{z^2}$  to the metal part of the ground state wave function.

The reason behind the above discrepancy between theory and experiment has been the subject of considerable interest,<sup>7-12</sup> particularly because a number of copper(II)-containing molecules of biological interest also show small values of  $A_z$ .<sup>12,13</sup> Sharnoff proposed that the apparently anomalous  $A_z$  value of pseudotetrahedral  $\text{CuCl}_4^{2-}$  is due to a significant contribution of metal  $p$  orbitals in the ground state<sup>7</sup>, but the  $p$ -orbital admixture required seems unreasonable and is at variance with an analysis of the optical spectra of pseudotetrahedral copper(II) compounds.<sup>8</sup> Later workers have concluded that  $P$  and, in particular,  $K$  are substantially reduced as compared with their values in other compounds,<sup>9,10,14</sup> and the low value of  $K$  has been interpreted in terms of a copper(II)  $3d-4s$  spin-polarization effect.<sup>9,14</sup> However, this seems unsatisfactory, at least as far as  $\text{Cs}_2\text{Zn}[\text{Cu}]\text{Cl}_4$  is concerned, as the  $b_1(xy)$  ground state and  $a_1(4s)$  orbitals are not coupled in the  $D_{2d}$  point group of this complex. Recently, Bencini et al. have suggested that the high covalency of the metal-ligand bonds is responsible for the discrepancy.<sup>11</sup> It was proposed that modified expressions for the  $g$  shifts should be used in the equations interpreting the hyperfine parameters, though this was not investigated quantitatively.

The purpose of the present note is to point out that the hyperfine parameters of pseudotetrahedral copper(II) complexes are not in fact anomalous once the contributions from the minor  $d$ -orbital components ( $d_{x^2-y^2}$ ,  $d_{xz}$ ,  $d_{yz}$  for the  $D_{2d}$  point group) of the ground state are properly included. This may be done by estimating  $C_1$  and  $C_2$  with eq 2, the values of  $\alpha^2$  being obtained from the analysis of ligand hyperfine parameters, and  $E_{x^2-y^2}$  (or  $E_{xy}$  if the ground state is  $d_{x^2-y^2}$ ) and  $E_{xy,yz}$  from electronic spectroscopy. The values of  $\beta^2$  and  $\gamma^2$  are not known directly and were set equal to one another and midway between  $\alpha^2$  and 1 in the present calculations, except for  $\text{Cu}(\text{NH}_3)_4^{2+}$ , where  $\pi$ -bonding was assumed absent with

$\beta^2 = \gamma^2 = 1$ ; changing  $\beta^2$  so that  $\alpha^2 - \beta^2$  varied by  $\pm 50\%$  altered the calculated hyperfine values by less than  $10 \times 10^{-4} \text{ cm}^{-1}$  in every case. The hyperfine values calculated by using eq 1a,b in this way are listed in Table I. For rhombically distorted  $(\text{enH}_2\text{Cl})_2\text{Zn}[\text{Cu}]\text{Cl}_4$  the relationships in eq 6 were used to derive expressions

$$\Delta g_z = \frac{-8\lambda k_z^2}{E_{xy}} \quad \Delta g_x = \frac{-2\lambda k_x^2}{E_{yz}} \quad \Delta g_y = \frac{-2\lambda k_y^2}{E_{xz}} \quad (6a)$$

$$C_1 = \frac{-\alpha^2 \beta^2 \lambda}{E_{xy}} \quad C_2 = \frac{-\alpha^2 \gamma^2 \lambda}{E_{yz}} \quad C_3 = \frac{-\alpha^2 \gamma^2 \lambda}{E_{xz}} \quad (6b)$$

for the hyperfine parameters in terms of the coefficients  $C_1$ ,  $C_2$ , and  $C_3$  exactly analogous to those in 1a,b. When it is remembered that a constant value of  $P$  and  $K$  have been assumed, it can be seen that agreement between the calculated and observed hyperfine parameters is now acceptable for complexes of all stereochemistries, including pseudotetrahedral. An important factor that is expected to influence metal hyperfine parameters is the contribution from the minor  $d$ -orbital components of the ground state, as represented by  $C_1$  and  $C_2$  in eq 1a,b. This is quite small for planar compounds such as  $\text{Cu}(\text{NH}_3)_4^{2+}$  but increases as axial coordination, or a distortion toward a tetrahedral geometry, causes the relevant excited states to drop in energy. In pseudotetrahedral  $\text{CuCl}_4^{2-}$  the contribution from admixtures of the excited  $d$  states just balances those due to the isotropic and dipolar terms, giving rise to a value of  $A_z$  close to zero. The reason why eq 4a,b and 5a-c do not give a good estimate of  $A_z$  in this complex is because, as has been shown by detailed calculations,<sup>15,16</sup> the  $g$  shifts in  $\text{CuCl}_4^{2-}$  are strongly influenced by ligand-based contributions and because their use in the hyperfine expressions leads to a significant underestimate of the effects of the excited  $d$  states admixed into the ground state. In other words, for this complex, and also to a lesser extent for pseudotetrahedral  $\text{Cu}(\text{Ph}_3\text{PO})_2\text{Cl}_2$ , the relationships  $k_z^2 \approx \alpha^2 \beta^2$  and  $k_{xy}^2 \approx \alpha^2 \gamma^2$  are not satisfied. This interpretation, which is essentially analogous to that proposed by Bencini et al.,<sup>11</sup> thus implies that the low  $A_z$  value of pseudotetrahedral  $\text{CuCl}_4^{2-}$  is not a direct result of its stereochemistry, but is due rather to the low energy of the excited  $d$  states in this complex (the first-order perturbation expressions used in eq 1, 4, and 5 become poorer approximations as  $E_{xy}$ , etc. approach  $\lambda$  in magnitude; however, even for  $\text{CuCl}_4^{2-}$  extending the equations to second order<sup>17</sup> only causes the estimates of  $A_z$  and  $A_{xy}$  to be altered by  $-20 \times 10^{-4}$  and  $3 \times 10^{-4} \text{ cm}^{-1}$ , respectively). This means that when the  $g$  shifts properly reflect the  $d$ -orbital participation in the ground state, as should presumably be the case for complexes of electronegative ligands with small spin-orbit coupling constants, then eq 4a,b and 5a-c should correctly represent the metal hyperfine parameters of compounds of pseudotetrahedral geometry. The EPR spectrum of pseudotetrahedral  $\text{CuF}_4^{2-}$  should provide a test of this prediction, and this is currently under investigation.

It may be noted that although the use of the coefficients,  $C_1$ ,  $C_2$ ,  $C_3$  (eq 6a,b) gives a much better estimate of the hyperfine parameters of  $(\text{enH}_2\text{Cl})_2\text{Zn}[\text{Cu}]\text{Cl}_4$  than eq 5a-c, agreement with experiment is still only fair. However, in this complex, the molecular symmetry is such that the metal  $4s$  orbital may contribute directly to the ground state, thus affecting the isotropic hyperfine interaction. A value of  $K = 0.35$  in the equations derived from eq 6a-c yields the estimates  $A_x = 82 \times 10^{-4} \text{ cm}^{-1}$ ,  $A_y = 31 \times 10^{-4} \text{ cm}^{-1}$ ,  $A_z = -2 \times 10^{-4} \text{ cm}^{-1}$ , in good agreement with experiment. This implies a contribution of  $K \approx 0.08$  due to direct  $4s$  participation. The effective value expected for unit unpaired spin density in a copper  $4s$  orbital has been estimated as  $KP = 0.2003 \text{ cm}^{-1}$ ,<sup>18</sup> so that the contribution  $KP\alpha^2 = 21.6 \times 10^{-4} \text{ cm}^{-1}$  in  $(\text{enH}_2\text{Cl})_2\text{Zn}[\text{Cu}]\text{Cl}_4$  implies a fractional unpaired spin density of  $\sim 0.011$  in the copper  $4s$  orbital. The  $4s$  orbital is coupled with

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$d_{z^2}$  by the low symmetry of the ligand field,<sup>19</sup> so that the 4s participation actually occurs via the  $d_{z^2}$  component of the groundstate. The metal hyperfine parameters of the tetragonally compressed  $\text{CuF}_6^{4-}$  ion are of interest in this context, as here the unpaired electron is located predominantly in  $d_{z^2}$ .<sup>20</sup> In this case the hyperfine parameters calculated by using eq 1c,d and the conventional  $g$  shift expressions (4c,d) are very similar, as is expected for a complex of a ligand of this kind, but both are in poor agreement with experiment (Table I). Satisfactory agreement may be obtained by using a value of  $K = 0.20$  ( $A_z = 85 \times 10^{-4}$ ,  $A_{xy} = 23 \times 10^{-4} \text{ cm}^{-1}$  via eq 1c,d) corresponding to a fractional unpaired spin density of  $\sim 0.032$  in the copper 4s orbital. The

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mixing coefficient of  $d_{z^2}$  in the ground state of  $(\text{enH}_2\text{Cl})_2\text{Zn}[\text{Cu}]\text{Cl}_4$  is  $b \approx 0.27$ .<sup>6</sup> However, it should be noted that a coefficient of  $b = 0.5$  corresponds to an orbital of the form  $d_{2x^2-z^2-y^2}$ , which is equivalent to  $d_{z^2}$ , with  $x$  defined as the symmetry axis.<sup>21</sup> The value of  $\sim 0.011$  estimated for the 4s orbital coefficient in the ground state of  $(\text{enH}_2\text{Cl})_2\text{Zn}[\text{Cu}]\text{Cl}_4$  thus implies a value of  $\sim (0.5^2/0.27^2) \times 0.014 = \sim 0.038$  for the mixing coefficient in the above unconventional  $d_{z^2}$  orbital, which is similar to that deduced for the axially symmetric  $\text{CuF}_6^{4-}$  complex.

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## Additions and Corrections

1984, Volume 23

**E. I. Onstott,\* Laura B. Brown, and E. J. Peterson\*:** Desolvation Method for Assessment of Crystallization Energies and Ion Crowding in Rare-Earth Perchlorates, Chlorides and Nitrates.

Page 2432. In Table I the second entry in the last column should read -1391. In Table III the saturated molality datum for dysprosium nitrate is in error; it should read 4.738 in column 2, according to a recent correction in the literature. (Spedding, F. H.; Derer, J. L.; Mohs, M. A.; Rard, J. A. *J. Chem. Eng. Data* **1985**, *30*, 242). We have recalculated data for dysprosium nitrate that should read as follows: column 3, 11.715; column 5, 0.5235; column 6, 0.175; column 7, 383; column 8, 2189. The last datum reveals that the work of crystallization in the nitrate series is a maximum for gadolinium nitrate rather than for dysprosium nitrate.—E. I. Onstott

**Joshua Telser and Russell S. Drago\*:** Reinvestigation of the Electronic and Magnetic Properties of Ruthenium Butyrate Chloride.

Page 3115. An error was discovered in the equation for the exponential form of the zero-field susceptibility for an  $O_h$ ,  $S = 3/2$  complex with axial zero-field splitting.<sup>1</sup> The correct equation for  $\chi_{\perp}$  ( $\chi_{\parallel}$  is correct as written) is as follows:

$$\chi_{\perp} = \frac{Ng_{\perp}^2\beta^2}{kT} \frac{4 + (3kT/D)(1 - \exp(-2D/kT))}{4(1 + \exp(-2D/kT))}$$

The magnetic susceptibility data were fitted by using this correct equation. This gave values of  $D = 70.6 \text{ cm}^{-1}$ ,  $g = 2.09$ , and  $g_{\perp} = 2.11$ . These are in much better agreement with values obtained previously by using the full spin Hamiltonian for an  $O_h$ ,  $S = 3/2$  system with axial zero-field splitting. In addition, the susceptibility data were fitted here by using the spin Hamiltonian, but allowing rhombic distortion. This gave  $D = 76.8 \text{ cm}^{-1}$ ,  $E = -0.007 \text{ cm}^{-1}$ ,  $g_z = 2.022$ ,  $g_x = 2.134$ , and  $g_y = 2.137$ . Within experimental error, these values are identical with those obtained with only axial distortion. A true axial system is also suggested by the crystallographic and EPR data.

Additional errors in the literature<sup>1</sup> equations for susceptibilities were discovered and the correct versions are given below:

for  $S = 1$

$$\chi_{\perp} = (Ng_{\perp}^2\beta^2/kT)\{(2kT/D) \times (1 - \exp(-kT/D))/[1 + 2 \exp(-kT/D)]\}$$

for  $S = 5/2$

$$\chi_{\perp} = (Ng_{\perp}^2\beta^2/kT)\{[9 + (4kT/D) \times (1 - \exp(-2D/kT)) + (9kT/2D)(\exp(-2kT/D) - \exp(-6kT/D))]/4(1 + \exp(-2kT/D) + \exp(-6kT/D))\}$$

Page 3118. By use of an EPR simulation program for  $S = 1/2$  systems, a value for  $A_{\perp}$  of  $26.7 \times 10^{-4} \text{ cm}^{-1}$  was obtained. However, this

is an effective  $A$  value,  $A^e$ , and must be converted to  $A_{\perp}$  for an  $S = 3/2$  system.<sup>2</sup> In this case,  $A^e_{\perp} = 2A_{\perp}$ , giving  $13.35 \times 10^{-4} \text{ cm}^{-1}$  as the correct value for  $A_{\perp}$ . This leads to  $A_{\text{iso}} = 16.13 \times 10^{-4} \text{ cm}^{-1}$  and  $A_{\text{dip}} = 2.78 \times 10^{-4} \text{ cm}^{-1}$ .

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—Joshua Telser, Vincent M. Miskowski, Russell S. Drago, and Ngai M. Wong

1985, Volume 24

**Leigh C. Porter and Robert J. Doedens\*:** Preparation and Crystal Structure of a Diamagnetic Copper(II) Trichloroacetate Complex Containing a Nitroxyl Radical Ligand.

Pages 1006, 1008. The nitroxyl ligand was named incorrectly. The correct name is 2,2,5,5-tetramethylpyrrolinyl-1-oxy.—Robert J. Doedens

**Wilmont F. Howard, Jr., Roger W. Crecey, and Wilfred H. Nelson\*:** Octahedral Dialkyltin Complexes: A Multinuclear NMR Spectral Solution Structural Study.

Page 2206. In Table IV, the last three columns were incorrectly printed because of a computer system error that occurred after the author had returned galley proof. The correct version of columns 4–6 is as follows:

<sup>1</sup> J( <sup>119</sup> Sn- <sup>13</sup> C), Hz	<sup>2</sup> J( <sup>119</sup> Sn-C- <sup>1</sup> H), Hz	ref <sup>a</sup>
977	99.3	10, 2
630	68.7	42, b
664	84.0	42, 23
664	84.0	43, 23
	81.6	28, 28
	81.5	29, 29
880	98.1	32, b

<sup>a</sup> First reference for X-ray data, second for NMR values. <sup>b</sup> This work.

—Wilmont F. Howard, Jr.

**F. Wudl,\* E. T. Zellers, and S. D. Cox:** Simplified Procedure for the Preparation of Metal Diselenolenes.

Page 2865: Reference 4 should read: Wudl, F.; Nalewajek, D. J. *Chem. Soc., Chem. Commun.* **1980**, 866 and references therein. Chiang, L.; Poehler, T. O.; Bloch, A. N.; Cowan, D. O. *Ibid.* **1980**, 866. Bolinger, C. M.; Rauchfuss, T. B. *Inorg. Chem.* **1982**, *21*, 3947. The latter describes the use of  $\text{Cp}_2\text{Ti}(\text{Se}_2\text{C}_2\text{R}_2)$  in the preparation of complexed ( $\text{L} = \text{Ph}_3\text{P}$ ,  $\text{Ph}_2\text{PC}\equiv\text{CPPH}_2$ ,  $\text{dppp}$ ,  $\text{CO}$ ) metal monodiselenolenes  $\text{L}_m\text{MSe}_2\text{C}_2\text{R}_2$  and potential preparation of  $\text{M}(\text{Se}_2\text{C}_2\text{R}_2)_2$ .—F. Wudl