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Spectral Studies of Bipyridyl and *o*-Phenanthroline Adducts of Divalent Metal Diketonates

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Powder e.s.r. spectra are reported for manganese(II) ions doped into Mg(hfac)$_2$L, Zn(acac)$_2$L (hfac = hexafluoro-acetylacetone, L = bipyridyl or o*-phenanthroline). Cd(acac)$_2$bipyridyl and Cd(acac)$_2$·*o*-phenanthroline·H$_2$O, and the zero-field splitting parameters D and λ (= E/D) are derived. Distortions from octahedral symmetry are greater for the bipyridyl than for the* o*-phenanthroline complexes, and greater for cadmium than for the other two metal ions. Infrared studies show all the complexes to be tris-bidentate except for Cd(acac)$_2$·*o*-phen·H$_2$O, which probably has a free carbonyl group and coordinated water.*

Introduction

As part of our investigations into the use of manganese(II) as a stereochemical probe for complexes of group(II) metal ions, we report here the infrared and e.s.r. powder spectra of some adducts of metal β-ketoenolates M^{II}(Mn)(diketone)$_2$L, where L represents 1,10-phenanthroline or 2,2′-bipyridyl. These complexes are expected generally to have *cis*-octahedral stereochemistry, the diimines being unable to span *trans*-positions in the complexes. The host complexes studied are listed in Table I.

Experimental

Mg(Mn)(hfac)$_2$phen·0.5H$_2$O

This was obtained as pale yellow crystals on mixing chloroform solutions of phen·H$_2$O and Mg(hfac)$_2$·3H$_2$O (+1 mol% Mn(Hfac)$_2$(H$_2$O)$_2$) in the stoicheiometric ratio; the fibrous *bipy* adduct was prepared similarly but from benzene solution.

Zn(Mn)(acac)$_2$(L) (L = phen, bipy)

Zn(acac)$_2$(H$_2$O)$_2$ [+1 mol% Mn(acac)$_2$(H$_2$O)$_2$] and an equimolar amount of the α-diimine were dissolved in chloroform and petroleum ether (60–80 °C) was added to incipient precipitation. Off-white crystals were obtained on overnight refrigeration of the solutions.

Cd(acac)$_2$(L) (L = phen, bipy)

An ethanolic solution of the α-diimine was added to an equimolar amount of Na[Cd(Mn)(acac)$_3$] in water. The finely divided white products were stirred for several minutes prior to filtration.

All spectra were obtained on polycrystalline samples at room temperature. The spectrometers have been described previously [1].

TABLE I. Analytical Results.

Compound	Found			Calculated		
	%C	%H	%N	%C	%H	%N
Mg(hfac)$_2$phen	42.5	2.0	4.4	42.7	1.6	4.5
Mg(hfac)$_2$bipy	40.5	2.3	4.4	40.4	1.7	4.7
Zn(acac)$_2$phen	59.6	5.5	5.8	59.5	5.0	6.3
Zn(acac)$_2$bipy	57.3	5.0	6.9	57.2	5.3	6.7
Cd(acac)$_2$phen·H$_2$O	52.0	4.7	5.6	51.9	4.8	5.5
Cd(acac)$_2$bipy	51.8	4.6	5.8	51.5	4.8	6.0

TABLE II. Selected Bands (cm^{-1}) in the IR Spectra of the phen Adducts.

phen•H_2O	Zn(acac)$_2$phen	Cd(acac)$_2$phen•H_2O	Assignments
–	540 m	540 v, br	ν(M–O)
620	635 m	636 m	phen: ring bend (?)[a]
727 s	720 m	721 sh	phen: ring-H o.o.p. bend
738 s	731 s	727 s	
751 m	761 s	764 m	phen: ring-H o.o.p. bend and acac: δ(C–H) o.o.p.
775 w	782 m	778 s	
830 s	849 s	847 s	phen: ring-H oo.o.p. bend
850 s	860 w	861 w	
1133 m	1138 v.w.	1146 m	phen: ring-H i.p. bend
1500 s	1505 s	1510 s	phen: ring stretch C=C + C=N and acac: ν(C=C) + ν(C=O)
1558 m			
1585 m		1585 s	
	1590 s, br		
1615 w		1605 s	
1640 w			
–	–	1675 m, sp	acac: uncoordinated ν(C=O)
3400 m, br		3400 m, br	H_2O: ν(O–H)

[a] phen bands assigned by analogy with bipy complexes.

TABLE III. Selected Bands (cm^{-1}) in the IR Spectra of the bipy Adducts.

bipy	Zn(acac)$_2$bipy	Cd(acac)$_2$bipy	Assignments
–	539 m	533 s	ν(M–O)
	542 m, sh		
618 m	625 m	625 m	bipy: ring bend
		732 m	bipy: ring-H o.o.p. bend and acac: δ(C–H) o.o.p.
736 s	739 m		
750 s, br	749 m		
	757 m		
	765 m	765 sh	
	771 s	771 s	
1135 m	1150 m, br	1152 m, br	bipy: ring-H i.p. bend
	1170 w	1170 w	
–	1310 m	1315 m	coordinated bipy (see text)
–	1510 s	1510 s	acac: ν(C=C)
~1552 s, split			acac: ν(C=O) and bipy: ring stretch C=C + C=N
1575 s		1575 s, br	
	~1595 s, br	1600 s, br	

TABLE IV. Selected Bands (cm^{-1}) in the IR Spectra of the Mg(II) Complexes.

Mg(hfac)$_2$•3H_2O	Mg(hfac)$_2$phen	Mg(hfac)$_2$bipy	Assignment
–	645 w	630 w	phen, bipy: ring bend
	725 sh		phen, bipy: ring-H o.o.p. bend
	731 s		
		738 m	
	741 w		
742 m			
	762 m	762 s	
771 w			
	798 m	795 s	hfac: ν(C–CF_3) + δ(CF_3)

(continued on facing page)

TABLE IV. *(continued)*

$Mg(hfac)_2 \cdot 3H_2O$	$Mg(hfac)_2$phen	$Mg(hfac)_2$bipy	Assignment
805 s		801 sh	
	810 w		
	852 m		
	870 w		
–	–	1315 m	coordinated bipy (see text)
1500 s, br		1508 s	
	1516 s		phen, bipy: ring stretch
	1532 s	1527 s	C=C + C=N
1545 s, br	1559 m	1552 m	
		1565 m	and
1570 s	1585 w	1575 m	
	1595 w	1595 m	
1617 m		1605 m	hfac: ν(C=C)
		1645 s	
1660 s	1659 s	1657 s	hfac: ν(C=O)
	1668 sh		
3400–3500 v. br.			H_2O: ν(O–H)

Infrared Spectra (4000–250 cm^{-1}) of the Complexes

The spectra are listed in Tables II–IV. Bands due to acetylacetone (acac) appear in virtually the same positions as in $M^I[M^{II}(acac)_3] \cdot nH_2O$ [2], indicating that with the exception of $Cd(acac)_2phen \cdot H_2O$ (see below) the diketones chelate in every case. Comparison of the spectra of the magnesium complexes with that of hexafluoroacetylacetone (hfac), leads to a similar conclusion for these complexes.

Extensive spectral studies of the free and coordinated diimines [3–7] have led to identification of the features diagnostic of the chelated ligands. The relevant observations in the present complexes are as follows. (i) Out-of-plane hydrogen deformations occurring between 700 and 850 cm^{-1} in the free ligands are split and/or shifted in the complexes. The spectrum of $Zn(acac)_2$bipy is distinguished by the multiplicity of bands in this region; this is consistent with the e.s.r. results which indicate the presence of more than one environment for the metal ion. (ii) The band at ~1315 cm^{-1} in the bipy adducts (which is absent in the free ligand) has been observed previously in several tris bipy complexes [5, 6]. (iii) The band at ~1135 cm^{-1}, ascribed to the ring-hydrogen in-plane bending vibration in both bipy and phen [6], is shifted to higher energy in the zinc and cadmium complexes (in the magnesium complexes, this region is obscured by the broad, strong C–F stretching vibration). (iv) The ring bending mode at ~620 cm^{-1} in the free diimines also moves to higher energy on complexation.

An interesting feature in the spectrum of $Mg(hfac)_2$bipy is the splitting of ν(C=O), both components of the doublet being of equal intensity. Splitting of comparable magnitude has been observed for ν(C=O) in $Zn(hfac)_2$bipy and $Zn(hfac)_2(py)_2$ [8] (a structural study [8] of the latter complex confirms that the hfac ligand is asymmetrically coordinated, and that the axial Zn–O distance is shorter than the in-plane bond length by 0.09 Å, the Zn–N distance being intermediate between the two values). In $Mg(hfac)_2$phen the higher energy component of ν(C=O) appears as a shoulder on the 1659 cm^{-1} band.

In the acac complexes ν(C=O) coincides with the diimine C=C and C=N vibrational frequencies, so that the mode of chelation of the diketone cannot be inferred from the IR data.

The presence of a band at 1675 cm^{-1}, assigned to 'free' C=O, in the spectrum of $Cd(acac)_2phen \cdot H_2O$ suggests monodentate coordination by at least one of the diketone molecules. Another distinctive feature of this spectrum is the breadth of the 540 cm^{-1} absorption, the half-width being about twice as large as in the other zinc and cadmium complexes. Coordinated water is reported to give a band at about this frequency [9], and it seems that this compound may contain one bidentate acac, one monodentate acac and one water molecule as the four oxygen donors. This arrangement, however, would still give rise to a *cis*-CdO_4N_2 arrangement, and since pyridine-type ligands appear to weaken donation from acac *trans* to them [8] replacement by a water molecule may make little difference to the electron spin resonance parameters.

E.s.r. Spectra of the Mn(II)-doped Complexes

Reference has been made previously [10] to the 'simplified' spin Hamiltonian for manganese(II) and the computer programs ESRS and SHAPE 9 employed in the spectral analysis. The labelling a–e of the fine structure transitions, and 1–6 of the spin levels, follows previous use [10].

TABLE V. X-band Esr Spectrum (mT) of Zn(Mn)(acac)$_2$phen; a, b, d and e Transitions.

Observed (ν = 9.535 GHz)	Calc. for D = 0.025 cm^{-1}, λ = 0.03		Calc. for D = –0.028 cm^{-1}, λ = 0.26		Calc. for D = 0.039 cm^{-1}, λ = 0.10	
	B	Axis, levels	B	Axis, levels	B	Axis, levels
123 w						
			221.9	a_z		
233 m	233.6	e_z	236.1	e_y		
					238.3	a_y
278 m			280.2	b_z		
284 s	284.8	a_y	286.3	d_y	283.5	b_y
	287.1	d_z				
	294.6	a_x			289.6	a_x
392 s	391.1	e_x	391.6	b_y	388.0	d_y
398 m	394.1	b_z	399.4	d_z		
	400.5	e_y			403.8	e_x
447 m	447.7	a_z	448.3	a_y	451.9	e_y
			461.0	e_z		

TABLE VI. Q-band Esr Spectrum (mT) of Zn(Mn)(acac)$_2$phen; a, b, d and e Transitions.

Observed (ν = 35.739 GHz)	Calc. for D = 0.025 cm^{-1}, λ = 0.03		Calc. for D = –0.028 cm^{-1}, λ = 0.26		Calc. for D = 0.039 cm^{-1}, λ = 0.10	
	B	Axis, levels	B	Axis, levels	B	Axis, levels
					1109.7	e_z
			1157.0	a_z		
1166 w	1169.6	e_z	1170.3	e_y	1169.3	a_y
					1193.1	d_z
1214 w	1218.9	a_y	1216.4	b_z		
					1220.0	a_x
1221 s	1223.1	d_z	1222.9	d_y	1221.1	b_y
	1228.6	a_x				
	1326.0	e_x				
1329 s	1330.2	b_z	1329.5	b_y	1329.5	d_y
1334 w	1335.5	e_y	1336.4	d_z	1336.7	e_x
					1360.1	b_z
1383 w	1383.7	a_z	1383.7	a_y	1386.3	e_y
			1396.8	e_z		
					1443.8	a_z

In Zn(Mn)(acac)$_2$phen spectral linewidths are high enough to result in severe overlapping between adjacent bands even at the extremities of the spectrum. Under these conditions, consideration of the a, b, d and e transitions, alone may not lead to unambiguous assignment of zfs parameters. In the present spectrum, the positions of the three pairs of bands flanking the central transition are consistent with (i) D = 0.025 cm^{-1}, λ = 0.03, or (ii) D = 0.028 cm^{-1}, λ = 0.26, or, less plausibly, with (iii) D = 0.039 cm^{-1}, λ = 0.10 (Table V and VI). Analysis of the X-band (4–3) transition was attempted to distinguish between (i) and (ii). The powder pattern for this transition (which is isotropic as far as terms linear in the fine structure parameters) has been calculated to second order, assuming an isotropic g-tensor and the absence of nuclear hyperfine interaction (Table VII).

In measuring the resonance fields in the experimental spectrum it has been assumed that second-order hf effects do not shift the centre of gravity of a sextet; it may be shown that such shifts for the c transition are $\leqslant$1 mT. Table VII also gives the values of B computed by exact diagonalization of the SPH matrix at the critical points, which agree well with the results of the perturbation calculations. The g_{eff} = 2 absorption pattern in the experimental spectrum corresponds closely to that predicted for D = 0.028

TABLE VII. Analysis of c(4–3) Transition in Zn(Mn)(acac)$_2$phen at X-band (field in mT).

Observed (ν = 9.535 GHz)	Perturbation calculations of powder pattern				Calculation of B by exact diagonalization of SPH matrix for D = 0.028 cm^{-1}, λ = 0.26
	D = 0.025 cm^{-1}, λ = 0.03		D = 0.028 cm^{-1}, λ = 0.26		
	B	Axis	B	Axis	
332.4 sh			331.8 sh	x	332.2
	335.7 sh	x			
	336.2 div	y			
337.6 div			337.3 sh	y	337.9
			338.3 div	xy pl. (θ = 90°, ϕ = 58°)	339.0
	340.2 sh	z	338.8 sh	z	339.3
343.8 sh or div			342.3 div	zx pl. (θ = 37°, ϕ = 0)	342.8
	347.0 div	zs pl. (θ = 41°, ϕ = 0)			
	348.4 sh	yz pl. (θ = 42°, ϕ = 90°)			
a			356.7 sh	yz pl. (θ = 44°, ϕ = 90°)	356.7

[a] Strong but poorly resolved absorption between 350 and 370 mT.

TABLE VIII. 5–2 Transition (mT) in the X-band Spectrum of Zn(Mn)(acac)$_2$phen.

Observed (ν = 9.535 GHz)	Calculated	
	D = –0.028 cm^{-1}, λ = 0.26	D = 0.025 cm^{-1}, λ = 0.03
104	104.3	99.3
112	111.6	106.4
119	119.8	114.3
127	128.7	122.8
137	138.4	132.1
147	148.9	142.2

cm^{-1}, λ = 0.26. This assignment is confirmed by the position of the only observed spin-forbidden band, centred on 122.9 mT and ascribed to the 5–2 transition in the yz plane. The predicted fields (corrected for higher order hf effects) for (i), (ii) and (iii) are 118.3, 124.2 and 127.3 mT. Table VIII compares the experimental and calculated (for (i) and (ii)) positions of the hf lines.

The spacing of the hyperfine components of the highest band is greater than that on the lowest allowed band. With the assignments of (ii) above, the highest field band must then be a_y and D is negative. For the other compounds the sign of D could not be determined, owing to the severe overlapping of transitions, or the incomplete resolution of the hyperfine structure. The band assignements are therefore given for positive D.

For Mg(Mn)(hfac)$_2$phen, accurate spin Hamiltonian parameters are not obtainable, as the linewidths of the outer transitions are even larger than those of Zn(Mn)(acac)$_2$phen. Analysis of the spectra is further complicated by the presence of a strong background signal, due possibly to absorption by aggregated Mn(II) ions. e_z and a_z occur at ~1154 and ~1410 mT at 35.84 GHz, giving a D value of *ca.* 0.03 cm^{-1}; this is consistent with the presence of a very weak signal centred on 470 mT at X-band. Location of a_y and e_y is more difficult, but estimates for λ of 0.17 or 0.22, obtained from the high field absorption (1379 or 1387 mT) at Q-band, were used to calculate the powder pattern of the c transition at 9.522 GHz.

TABLE IX. c(4–3) Transition (mT) of Mg(Mn)(hfac)$_2$phen at X-band.

Observed (ν = 9.522 GHz)	Calculated		Field direction
	D = 0.03 cm^{-1}, λ = 0.17	D = 0.03 cm^{-1}, λ = 0.22	
332.1 sh	331.5 sh	330.7 sh	x
334.5[b]	335.6 sh	336.1 sh	y
	335.8 div	336.8 div	xy pl.
338.4[b]	339.1 sh	338.6 sh	z
	345.1 div	343.5 div	zx pl.
a	356.1 sh	357.7 sh	yz pl.

[a] Strong but poorly resolved absorption to ~380 mT. [b] Not clear whether sh or div.

TABLE X. Q-band Esr Spectrum (mT) of Mg(Mn)(hfac)$_2$-bipy.

Observed (ν = 35.750 GHz)	Calculated for D = 0.079 cm^{-1}, λ = 0.24	
	B	Axis, levels
454 w		
624 w		
941 ms	940.5	e_z
990 ms	990.5	a_y
1107 s	1106.9	d_z
1127 s	1128.8	b_y
1419 s	1417.6	d_y
1444 s	1444.2	b_z
1573 ms	1570.5	e_y
1620 ms	1616.4	a_z

TABLE XI. Q-band Esr Spectrum (mT) of Cd(Mn)(acac)$_2$-phen•H$_2$O.

Observed (ν = 35.865 GHz)	Calculated for D = 0.078 cm^{-1}, λ = 0.17	
	B	Axis, levels
946 w	948.0	e_z
1031 w	1033.8	a_y
1112 ms	1113.6	d_z
1152 s	1151.6	b_y
	1207.3	a_x
1231 s	1231.6	b_x
1400 s	1401.7	d_y
1448 s	1447.3	b_z
1538 w	1536.3	e_y
1616 w	1615.8	a_z

TABLE XII. Q-band Esr Spectrum (mT) of Cd(Mn)(acac)$_2$-bipy.

Observed (ν = 35.88 GHz)	Calculated for D = 0.163 cm^{-1}, λ = 0.15	
	B	Axis, levels
593 m	588.5	e_z
803 m	804.5	a_y
933 m	932.8	d_z
1018 m	1020.4	b_y
	1125.6	a_x
1149 m	1152.9	b_x
1219 s	1219.5	c_x
1249 s	1250.9	c_y
1331 s	1330.8	d_x
+absorption to 1400	1498.2	e_x
1504 m	1505.0	d_y
1625 m	1626.9	b_z
1802 w	1798.0	e_y
1987 vw	1981.0	a_z

As Table IX shows, the lower of the two values of λ gives results in moderately good agreement with the experimental data.

X-band resonance fields for Mg(Mn)(hfac)$_2$bipy and Cd(Mn)(acac)$_2$phen·H$_2$O are not tabulated, as fine structure is poorly resolved, except in the case of a moderately intense transition at 160.9 mT (g_{eff} = 4.23). However, the zero field splitting parameters are readily evaluated from Q-band spectra (Tables X and XI) D/hν at 36 GHz being sufficiently low that perturbation theory may be usefully applied. These parameters in turn were used to calculate the X-band lineshapes, the experimental spectrum being generally well fitted.

Likewise for Cd(Mn)(acac)$_2$bipy, the zero field splitting parameters were calculated from the Q-band spectrum (Table XII) and used to reproduce the X-band lineshape.

The spectral profile at X-band of Zn(Mn)(acac)$_2$-bipy resembles those of Na[Zn(Mn)(acac)$_3$]·H$_2$O and M(Mn)(4Me-pyo)$_6$(ClO$_4$)$_2$ (M = Zn, Cd, or Hg) [10, 11], with D ~ 0.06 cm^{-1}. However, many more lines are observed than can be accounted for by a single set of SPH parameters; in addition, the lack of structure on the strong central band contrasts with the well resolved hyperfine lines of the corresponding transition in Na[Zn(Mn)(acac)$_3$]·H$_2$O. Both features are consistent with the presence of manganese ions in more than one environment. Severe overlapping of some adjacent lines at X-band precludes accurate measurement of all resonance fields. At Q-band, however, at least four pairs of transitions at the extremities of the spectrum are well resolved. Their positions and intensities appear to indicate roughly equal distribution of manganese ions between two lattice sites characterised by the parameters (i) D = 0.061 cm^{-1}, λ = 0.08 and D = 0.071 cm^{-1}, λ = 0.09 *or* (ii) D = 0.061 cm^{-1}, λ = 0.16 and D = 0.071 cm^{-1}, λ = 0.03 (Table XIII). X-band spectra were simulated, assuming equal numbers of manganese ions in the two environments, for both (i) and (ii); each closely resembles the experimental lineshape. A well-defined 'half-field' spectrum was observed in the usual region (100–150 mT) but owing to the very large number of spin-forbidden lines predicted for two sets of SPH parameters, it was not possible to make a clear distinction between (i) and (ii) on this basis.

Discussion

In both the bipyridyl and the *o*-phenanthroline series, the D values for the magnesium and the zinc host lattices are similar (Table XIV). In each case, however, the cadmium compound gives a much larger

TABLE XIII. Q-band Spectrum (mT) of Zn(Mn)$(acac)_2$bipy.

Observed (ν = 35.52 GHz)	Calculated			
	D = 0.061 cm^{-1}, λ = 0.16	D = 0.071 cm^{-1}, λ = 0.03	D = 0.061 cm^{-1}, λ = 0.08	D = 0.071 cm^{-1}, λ = 0.09
965 w		964.7 e_z		964.9 e_z
1006 w	1008.0 e_z		1007.6 e_z	
1075 w	1077.2 a_y			1079.4 a_y
1108 m		1108.2 a_y	1110.2 a_y	1116.6 d_z
		1116.8 d_z		
1127 m				
	1137.9 d_z	1136.0 a_x	1138.1 d_z	
				1164.8 a_x
[a]1183 vbr	1169.2 b_y	1181.4 b_y	1173.8 b_y	1168.0 b_y
	1206.9 a_x	1194.4 b_x	1184.8 a_x	1207.7 b_x
			1214.7 b_x	
[a]1337 vbr	1339.8 e_x	1331.3 d_x	1313.1 d_x	1316.4 d_x
	1362.7 d_y	1345.6 d_y	1345.8 e_x	1360.4 d_y
			1371.6 d_y	1383.7 e_x
1422 m	1399.0 b_z	1411.4 e_x	1399.3 b_z	1420.6 b_z
		1420.9 b_z		
1434 m		1438.2 e_y	1433.2 e_y	
1462 w	1465.3 e_y			1465.9 e_y
1527 vw	1530.4 a_z		1530.2 a_z	
1571 w		1573.0 a_z		1573.1 a_z

[a] Flanked by other, less well-resolved lines.

TABLE XIV. Zfs Parameters’ of Mn(II) in some Chelate Complexes.

Complex		D (cm^{-1})	λ
Mg$(hfac)_2$phen		0.03	0.17
Mg$(hfac)_2$bipy		0.079	0.24
Zn$(acac)_2$phen		−0.028	0.26
Zn$(acac)_2$bipy		0.061	0.08
	(i)	{	}
		0.071	0.09
	or		
	(ii)	0.061	0.16
		{	}
		0.071	0.03
Cd$(acac)_2$phen•H_2O		0.078	0.17
Cd$(acac)_2$bipy		0.163	0.15

[a] Errors in D and λ are estimated at ±0.01 cm^{-1} and ±0.03 for Mg$(hfac)_2$phen and ±0.001 cm^{-1} and ±0.01 for the other compounds.

D value. This is opposite to the trend expected from ionic size, since normally D decreases with increasing size of the host metal ion [10, 12, 13]. This raises the possibility that in this case there is a geometric distortion of the octahedra, such as the trigonal distortion found for KCd$(acac)_3$•H_2O, which also gives a very high D value for manganese [11].

For all three host metal ions, the bipyridyl complexes give much larger D values than the *o*-phenanthroline. The latter give surprisingly low values, comparable with those in *cis*-M$(acac)_2$(O-donor)$_2$.

The negative sign of D found for Zn$(acac)_2$phen heightens this analogy. It is thought [14] to imply that the octahedron is compressed along the major axis. This again is surprising for a *cis*-MO_4N_2 system, though Zn$(hfac)_2$pyridine$_2$ shows this geometry, the oxygen donors *trans*- to the nitrogens having unusually long M–O bonds. It seems likely that Zn$(acac)_2$phen has a similar structure.

It also appears that manganese(II) is a better probe for host-lattice geometry than is copper(II). The e.p.r. spectrum of Cu(II) in Zn$(hfac)_2py_2$ indicates a tetragonally elongated environment, as found for the pure copper complex, rather than the compressed octahedron of the host lattice [15].

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