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Metal Chelates of Heterocyclic Nitrogen-Containing Ketones. XI. Copper(II) Complexes of Syn-2-picolyl Phenyl and Syn-2-picolyl Methyl Ketoximes

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The reaction products of copper(II) salts with syn-2-picolyl phenyl ketoxime, HL, and syn-2-picolyl methyl ketoxime, HL', were investigated by analyses, magnetic susceptibility, ESR, reflectance and IR spectral measurements. Chelates of the type [(HL)-(L)Cu]X and [(HL')(L')Cu]X, X = Cl, Br, I, ClO_4, NO_3 or SCN were separated. The spectral data support the suggestion that these complexes possess square planar [(HL)(L)Cu]$^+$ and [(HL')(L')Cu]$^+$ groups and that these groups are linked by weakly coordinated anions. The complexes [(HL)$_2$Cu]$SO_4\cdot 2H_2O$ and [(HL')$_2$Cu]$SO_4\cdot 2H_2O$ appear to have a less tetragonally distorted structure.

Introduction

Due to their analytical uses, especially in gravimetric and solvent extraction analytical methods, the coordination chemistry of ketoxime and aldoxime compounds were subjected to extensive studies [1–7]. Although a variety of oximes have been studied over the past 30 years because of their reactivity towards metal ions [3–7], the metal complexes of syn-2-picolyl phenyl and syn-2-picolyl methyl ketoximes have not been quoted in the literature. In the continuation of our studies on chelating properties of the heterocyclic nitrogen containing ketones and their Schiff bases [8–12], the present work describes the preparation and characterization of copper(II) chelates with the derived oximes.

Experimental

Preparation of the Organic Ligands

The syn-ketoximes were prepared by direct oximation of 2-picolyl phenyl ketone and 2-picolyl methyl ketone with hydroxylamine sulphate according to the method given by Drago *et al.* [5]. The ketones were prepared according to the method given in our previous papers [9, 10]. The compounds were established by elemental analysis and physical properties (HL had m.p. 198 ± 1 °C and HL', m.p. 138 ± 1 °C).

Preparation and Analysis of Copper(II) Complexes

Monohydrogen-bis(syn-2-picolyl phenyl ketoxime) copper(II)X and monohydrogen-bis(syn-2-picolyl methyl ketoxime)copper(II)X; X = Cl or Br

A solution of copper(II) chloride dihydrate or copper(II) bromide dihydrate (0.01 mol) in ethanol (25 ml) was added to 0.02 mol of the corresponding ketoxime in ethanol (20 ml). The reaction mixture was boiled under reflux for an hour. On cooling to room temperature, green crystalline solids were separated, filtered off, washed with ethanol, and dried under vacuum over P_2O_5.

Monohydrogen-bis(syn-2-picolyl phenyl ketoxime) copper(II)NO_3 and monohydrogen-bis(syn-2-picolyl methyl ketoxime)copper(II)NO_3

0.02 mol of HL or HL' in ethanol (25 ml) was treated with 0.01 mol of copper(II) nitrate trihydrate in ethanol (25 ml). The reaction mixture was refluxed for one hour. A green polycrystalline solid was obtained immediately, filtered off, washed with ethanol, and dried in vacuum over P_2O_5.

Monohydrogen-bis(syn-2-picolyl phenyl ketoxime) copper(II)X and monohydrogen-bis(syn-2-picolyl methyl ketoxime)copper(II)X; X = I or SCN

0.02 mol of solid KI or KSCN was added to 0.02 mol of a suspension of the nitrate complex in hot ethanol (50 ml). An immediate reaction was observed yielding yellowish-green and pale green crystalline solids respectively. The reaction products were filtered, washed several times with ether, and dried in vacuum over P_2O_5.

Dihydrogen-bis(syn-2-picolyl phenyl ketoxime) copper(II) sulphate dihydrate and dihydrogen-bis(syn-2-picolyl methyl ketoxime)copper(II) sulphate dihydrate

To a solution of 0.02 mol HL or HL' in ethanol (30 ml), 0.01 mol of copper(II) sulphate pentahydrate

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TABLE I. Analytical Data.

	Compound	(Found), Calculated				
		%C	%H	%N	%Cu	%X
1	$[(HL)(L)Cu]Cl$	61.66 (61.60)	4.55 (4.60)	11.07 (11.00)	12.56 (12.53)	7.02 (7.12)
2	$[(HL)(L)Cu]Br$	56.67 (56.71)	4.18 (4.14)	10.17 (10.21)	11.54 (11.57)	14.53 (14.59)
3	$[(HL)(L)Cu]I$	52.22 (52.17)	3.85 (3.90)	9.37 (9.33)	10.63 (10.61)	21.25 (21.30)
4	$[(HL)(L)Cu]ClO_4$	54.73 (54.80)	4.03 (4.00)	9.82 (9.91)	11.14 (11.16)	6.23 (6.25)
5	$[(HL)(L)Cu]NO_3$	58.59 (58.61)	4.32 (4.36)	13.14 (13.08)	11.93 (12.00)	–
6	$[(HL)(L)Cu]NCS$	59.03 (58.94)	4.35 (4.40)	13.24 (13.20)	12.02 (11.98)	S = 6.05 (6.11)
7	$[(HL)_2Cu]SO_4 \cdot 2H_2O$	51.17 (51.22)	4.64 (4.68)	9.28 (9.36)	10.53 (10.49)	S = 5.30 (5.24)
8	$[(HL')(L')Cu]Cl$	48.24 (48.16)	4.77 (4.71)	14.07 (14.00)	15.96 (16.00)	8.92 (8.85)
9	$[(HL')(L')Cu]Br$	43.39 (43.45)	4.29 (4.28)	12.65 (12.60)	14.36 (14.40)	18.08 (18.00)
10	$[(HL')(L')Cu]I$	39.22 (39.27)	3.88 (3.81)	11.44 (11.38)	12.98 (13.00)	25.94 (25.99)
11	$[(HL')(L')Cu]ClO_4$	41.55 (41.60)	4.11 (4.06)	12.12 (12.19)	13.75 (13.81)	15.15 (15.03)
12	$[(HL')(L')Cu]NO_3$	45.23 (45.18)	4.48 (4.51)	16.49 (16.43)	14.97 (15.00)	–
13	$[(HL')(L')Cu]NCS$	45.66 (45.73)	4.52 (4.47)	16.65 (16.72)	15.11 (15.18)	S = 7.61 (7.71)
14	$[(HL')_2Cu]SO_4 \cdot 2H_2O$	40.04 (40.12)	5.00 (4.93)	11.68 (11.59)	13.25 (13.28)	S = 6.16 (6.20)
15	$[(HL)(L)Cu]HSO_4$	53.47 (53.51)	4.11 (4.08)	9.59 (9.57)	10.89 (10.87)	S = 5.48 (5.51)
16	$[(HL')(L')Cu]HSO_4$	41.78 (41.77)	4.35 (4.38)	12.19 (12.12)	13.83 (13.81)	S = 6.96 (7.00)

in water (25 ml) was added. The reaction mixture was refluxed for 8 hours. On keeping the reaction mixture at room temperature overnight, a light green crystalline solid separated. The product was filtered, washed with water and ethanol, and dried in vacuum over P_2O_5.

Copper(II) and sulphur contents were determined as given in our previous publication [8, 9, 11]. Carbon, nitrogen and hydrogen contents were estimated at the Microanalytical Laboratory at Cairo University, Cairo, Egypt. The data are given in Table I.

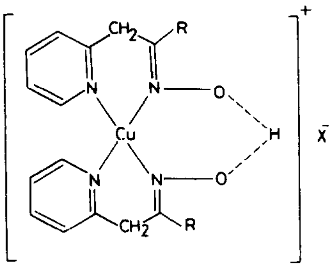
Physical Measurements

The diffused reflectance spectra were recorded with a CARY 14 spectrophotometer. IR spectra were measured using KBr discs with a UNICAM SP 2000 spectrophotometer. ESR data were obtained with a VARIAN spectrometer in the solid state as polycrystalline solids at X-band and DPPH was used as reference. Magnetic measurements were carried out at room temperature using the Gouy method, and the diamagnetic corrections were calculated by the use of Pascal's constants [14].

Results and Discussion

The IR spectra of free ligands HL and HL' exhibit multicomponent bands in the 3000–2820 cm^{-1} range which are assigned to the intermolecular hydrogen bonded OH of the oxime groups [15]. The νC–H stretching vibrations are obscured by the νOH absorptions.

The [(HL)(L)Cu]X and [(HL')(L')Cu]X complexes exhibit strong broad bands in the 3540–3510, 3440–3420 and 3100–3020 cm^{-1} regions which are assigned to the free νOH, H-bonded OH and νC–H stretching vibrations of the ligands respectively [4, 5, 16]. The broad OH stretching frequency near 3400–3200 cm^{-1} region is absent in all complexes, indicating the ionization of one proton of the oxime groups [1, 2, 13]. Furthermore, the strong band near 1600 cm^{-1} attributed by Liu *et al.* [1] to OH stretching of hydrogen bonded group is exhibited by all the complexes. The free ligands exhibit the νC=N (acyclic) and νN–O at 1620–1610 and 990–980 cm^{-1}, respectively. The νC=N(acyclic) vibrational band is shifted to lower frequency by *ca.* 15–20 cm^{-1} and is obscured by pyridine band of the ligand molecules in the complexes. The νN–O vibrational band is shifted to higher frequency, by *ca.* 20–25 cm^{-1}. The νC=N(cyclic) in the free ligands appeared at 1590–1580 cm^{-1} which on coordination is shifted to lower frequency by *ca.* 10–15 cm^{-1}, and may overlap with the νC=N(acyclic). The δPy appeared at 630 cm^{-1} in the free ligands, and shifted to higher frequency with splitting on complex formation. According to the IR data and the observation in our previous paper [13], the ligands act as monobasic or neutral bidentate giving chelates as shown in Fig. 1.



R = Me or Ph, X = Cl^-, Br^-, I^-, NO_3^-, ClO_4^- or SCN^-

Fig. 1. Structure of complexes.

The nitrate-containing complexes exhibit bands at 1360, 1315 and 820 cm^{-1} and a very broad band at 1030 cm^{-1}. The ν_2 (820 cm^{-1}) is close to that expected for an ionic nitrate, and while the ν_3 band (1360, 1315 cm^{-1}) shows clear evidence of splitting, the separation of the components is not as great as is normally observed for mono- or bidentate nitrate groups [4, 17]. The ν_3 band is split to an extent comparable to that observed in $Cu(en)_2(NO_3)_2$, in which the molecular structure determination has shown the nitrate groups to be only weakly coordinated [18]. Therefore, the spectrum is best considered as indicating weak semi-coordination of the nitrate group.

The sulphate-containing complexes exhibit bands at 1050 (ν_1), 980–1000 (ν_2), 590–580 (ν_3), 480–525 (ν_4), 1170 (ν_5), 610–615 (ν_6), 1075–1080 (ν_7) and 640–650 (ν_8) cm^{-1}. The presence of ν_{S-O} at 980–1000 cm^{-1} and other bands indicate the bidentate nature of sulphate groups in these complexes [17, 19].

The perchlorate-containing complexes exhibit bands at *ca.* 1125, 1020 cm^{-1} together with a weak band at 940 cm^{-1}, which indicates the monodentate semicoordinating nature of the perchlorate group [17, 19].

The IR spectra of the thiocyanate complexes show a series of bands at *ca.* 2130 (νCN), 820 (νCS) and 480 (δNCS), which are characteristic of the monodentate N-bonded thiocyanate group [19].

In the far IR spectra, the free ligands exhibit bands at 400, 330, 295, 280, 250 and 225 cm^{-1}. These bands appear at 405–380, 295–280 and 250–245 cm^{-1} in their copper(II) complexes, and are assigned to the ligands absorption bands. The νCu–N vibration modes in all complexes appear at 350–360 cm^{-1} and another medium one at 300 cm^{-1}. The sulphate-containing complexes exhibit the νCu–N bands at 345–340, 320 and 270–260 cm^{-1}.

Magnetic and Spectral Studies

The room temperature magnetic moments, Table II, of the copper(II) complexes lie in the range 1.85–1.94 B.M. The values are found to slightly decrease on decreasing the temperature to 77 °K and obev the Curie–Weiss law [11] with very small Weiss constant (θ) values. The magnetic data indicate that these complexes have an orbitally non-degenerate B-type ground state [10, 17]. Furthermore, the decrease of the magnetic moments with decreasing temperature and the values higher than the spin-only (1.73 B.M.) value at room temperature implies the presence of the low-lying excited states which at room temperature are able to mix-in some of their orbital angular momentum into the ground state through spin–orbit coupling, common for copper(II) complexes with distorted ligand fields [10, 17, 20, 21]. The temperature variation of the magnetic susceptibility of these complexes will be clarified in another study.

The reflectance spectra of [(HL)(L)Cu]X and [(HL')(L')Cu]X complexes, where X = Cl, Br, I, ClO_4, NO_3 and SCN, at room temperature are listed in Table II. Except for the sulphate containing complexes, all show broad, intense maxima in the region 17400–18900 cm^{-1} together with a well-defined shoulder in the region 14250–16650 cm^{-1}. The spectra are similar to those reported for copper(II) ion in either an essentially square co-planar environment or in an octahedral environment with a very strong tetragonal distortion [4, 10, 21]. In the tetragonal environment, three principal bands are expected but only a few complexes are known in which such bands have been resolved and assigned to the ${}^2B_{1g} \rightarrow {}^2A_{1g}$, ${}^2B_{1g} \rightarrow {}^2B_{2g}$, and ${}^2B_{1g} \rightarrow {}^2E_g$ transitions in order of increasing energy [21]. The low

TABLE II. Magnetic, Electronic and ESR Spectral Data.

Compound	μ_{eff}* (B.M.)	Electronic Spectral Data (cm^{-1})	ESR Data				
			$g_{\parallel}$	$g_{\perp}$	$g_{av.}$		R
1	1.85	17400, 14300	2.240	2.068	2.125		2.52
2	1.87	17540, 14530		2.130			
3	1.89	17970, 14670	2.240	2.065	2.123		3.69
4	1.88	17700, 14730	2.241	2.068	2.126		3.54
5	1.91	18560, 15105	2.247	2.070	2.129		3.52
6	1.94	18900, 16080	2.245	2.070	2.127		3.50
7	1.87	12900–14900br, 8995	2.010	2.200	2.136		
8	1.85	17500, 14680	2.246	2.070	2.126		3.51
9	1.88	17560, 14700		2.135			
10	1.89	17990, 14805	2.250	2.073	2.132		3.42
11	1.91	17770, 14680	2.246	2.071	2.129		3.46
12	1.93	18580, 15080	2.247	2.076	2.133		3.25
13	1.92	18890, 16320	2.253	2.078	2.136		3.24
14	1.87	12800–14780br, 9000	2.020	2.190	2.153		
			g_1	g_2	g_3	$g_{av.}$	G
15	1.88	14800, 12900	2.041	2.099	2.140	2.09	0.53
16	1.87	14850, 12900	2.052	2.093	2.177	2.11	0.43

*Measured at room temperature (23 ± 1 °C).

energy shoulder in the present complexes is assigned to the $^2B_{1g} \rightarrow {}^2A_{1g}$ transition and the main spectral band is assigned to $^2B_{1g} \rightarrow {}^2E_g$ transition [21]. Evidence that the anion is weakly coordinated is obtained from the dependence of the reflectance spectra on the anion and the above-mentioned IR data from the anions. Therefore it seems likely that these complexes have chain structures with the anion bridging between the square planar $[(HL)(L)Cu]^+$ and $[(HL')(L')Cu]^+$ units, as the reflectance spectra are not consistent with those expected for a square pyramidal or trigonal bipyramidal structures for these complexes [17, 21, 22].

The $[(HL)_2Cu]SO_4 \cdot 2H_2O$ and $[(HL')_2Cu]SO_4 \cdot 2H_2O$ complexes display spectral features with maxima at *ca.* 12900–14900 and 12800–14780 cm^{-1} respectively, these being beside another band at *ca.* 8995 and 9000 cm^{-1} for the two complexes respectively. These spectral features are very similar to those reported for $[(biPy)_2Cu\,ONO]^+$, which has been shown by X-ray studies to have a distorted *cis*-octahedral structure [23]. It has been suggested that the occurrence of two equally intense bands separated by *ca.* 5000 cm^{-1}, can be used to distinguish a distorted *cis*-octahedral from that of trigonal-bipyramidal stereochemistry, wich is characterised by a single peak split by less than 3000 cm^{-1}. In these sulphate-containing complexes, water molecules may be bonded to the oxime group, in some way preventing the formation of square planar units where their IR data gave no evidence for the $[(HL)(L)Cu]^+$ or $[(HL')(L')Cu]^+$ units. Representative spectra are shown in Figs. 2, 3.

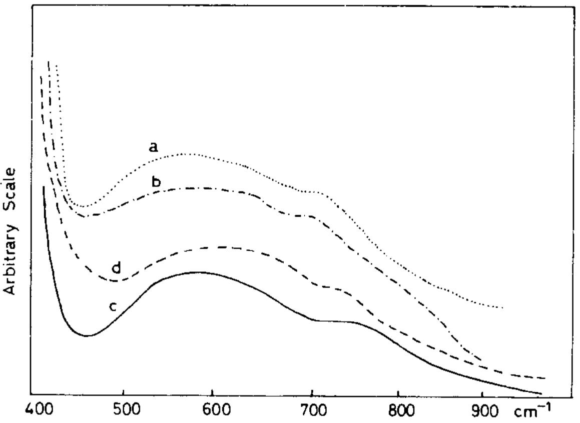


Fig. 2. The electronic spectra of: a) [(HL)(L)Cu]Cl; b) [(HL)(L)Cu]ClO$_4$; c) [(HL')(L')Cu]Cl; d) [(HL')(L')Cu]-ClO$_4$.

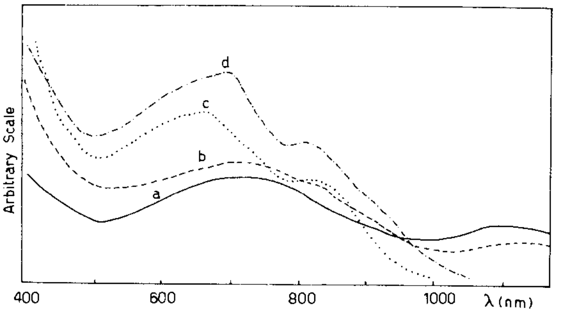


Fig. 3. Electronic spectra of: a) [(HL)$_2$Cu]SO$_4$·2H$_2$O; b) [(HL')$_2$Cu]SO$_4$·2H$_2$O; c) [(HL)(L)Cu]HSO$_4$; d) [(HL')(L)-Cu]HSO$_4$.

The X-band ESR spectra of the polycrystalline complexes, [(HL)(L)Cu]X and [(HL')(L')Cu]X; X = Cl, I, NO_3, ClO_4 or SCN, at 25 °C are typical of those reported for axial type copper(II) complexes [24, 25], with two g-values, $g_{\parallel} > g_{\perp} > 2.00$. Typical spectra are shown in Fig. 4 and the results are given in Table II. In an axial symmetry, the g-values are related by the expression, $G = (g_{\parallel} - 2)/(g_{\perp} - 2)$, which measures the extent of interaction between copper(II) centers in the polycrystalline solid [17]. According to Hathaway [18], the value of G is larger than four and the exchange interaction is negligible; when G is less than four a considerable exchange interaction in the solid complexes is present. The calculated G-values are given in Table II. The average g-values were calculated according to the relation, $g_{av.} = 1/3 g_{\parallel} + 2/3 g_{\perp}$, gave values in the range 2.125–2.136 which are in agreement with an orbitally non-degenerate ground state.

The ESR spectra of the bromide-containing complexes are characterized by one broad signal and $\Delta_{peak-peak} = 610$ gauss, Fig. 4. These isotropic ESR spectra are most commonly due to the dipolar broadening and enhanced spin lattice relaxation of the bromide ion [24].

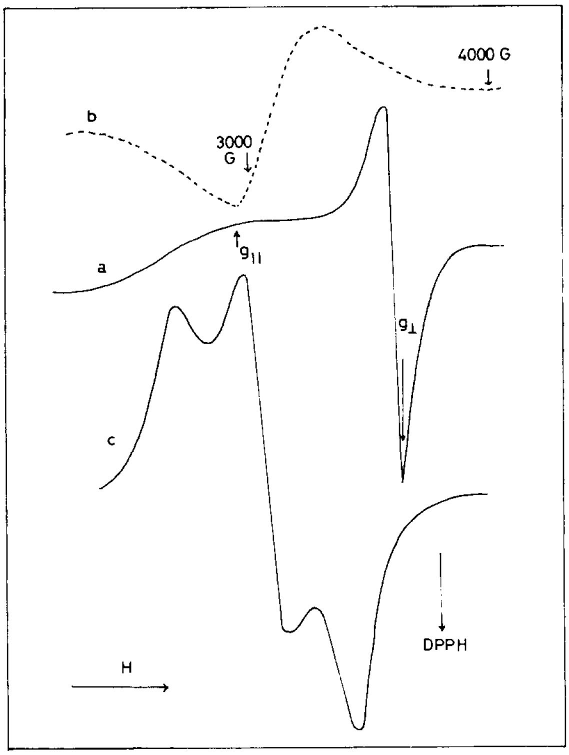


Fig. 4. The X-band ESR spectra of: a) [(HL)(L)Cu]Cl; b) [(HL)(L)Cu]Br; c) [(HL)(L)Cu]HSO_4 at 25 °C.

The ESR spectra of [$(HL)_2Cu$]$SO_4 \cdot 2H_2O$ and [$(HL')_2Cu$]$SO_4 \cdot 2H_2O$ complexes are very similar and are characteristic [25] of a complex with two g-values and with $g_{\perp} > g_{\parallel} \simeq 2.00$, Fig. 5 and Table II. This together with the lower g-value being close to 2.00, suggests a d_{z^2} orbital as the ground state [26]. A d_{z^2} ground state is predicted for either a compressed-tetragonal, trigonal bipyramidal or *cis*-octahedral stereochemistry around the copper(II) ion [26]. Thus from the ESR and electronic spectra of the sulphate-containing complexes, an approximately *cis*-octahedral structure is suggested for these complexes.

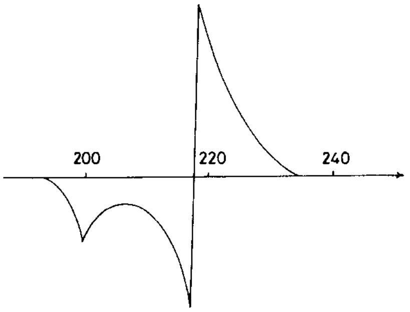


Fig. 5. The first-derivative ESR spectrum of [$(HL)_2Cu$]$SO_4 \cdot 2H_2O$.

The products obtained by dehydration of [$(HL)_2$-Cu]$SO_4 \cdot 2H_2O$ and [$(HL')_2Cu$]$SO_4 \cdot 2H_2O$ have the –C=N– and –N–O– absorption bands in their IR spectra in the regions 1550 and 1130 cm^{-1} respectively. These vibrational bands are expected for compounds containing the square planar [(HL)(L)Cu]$^+$ and [(HL')(L')Cu]$^+$ units. The IR spectra of these complexes exhibit bands at 1175s, 1150s, 1035s, (broad band), 970m, 620w, 610vw and 448w cm^{-1} which are attributed to the HSO_4 group vibrational modes [4]. These IR bands indicate the monodentate nature of the HSO_4 group in these complexes [4].

The reflectance spectra of the dehydrated sulphate-containing complexes exhibit spectral features with maxima at 14900–14750 cm^{-1} with a well-traced shoulder at 13000–12780 cm^{-1}. The shape and the band positions suggest that copper(II) ion is in a square-pyramidal ligand field stereochemistry [8, 21, 22]. The ESR spectra of these complexes as polycrystalline solid in the X-band at 25 °C are anisotropic. The spectra gave three g-values, $g_1 < g_2 < g_3$. The average g-values were calculated from the relation, $g_{av.} = 1/3(g_1 + g_2 + g_3)$ and listed in Table II. In this system the g-values are related with the factor R which is defined by the ratio, $(g_2 - g_1)/(g_3 - g_2)$. If the value of R is greater than one then a predominantly d_{z^2} ground state is present, while for a $d_{x^2-y^2}$ ground state, R is expected to be less than one. The calculated R values given in Table II indicate a $d_{x^2-y^2}$ ground state which is consistent with a square-based pyramidal structure, in agreement with the electronic absorption spectra. However, since the crystal structures of these complexes are not known, we cannot conclude to what extent the g-values reflect the actual molecular structures.

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