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Cobalt(II), Copper(II) and Zinc(II) Complexes of some Bidentate Imidazoline, Benzimidazole and Benzothiazole Ligands

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Complexes of cobalt(II), copper(II) and zinc(II) with some bidentate ligands involving the pseudo-imidazole functional groups imidazoline, benzimidazole and benzothiazole are described; $M(BBTE)X_2$ *(*$M = Co, X = Cl, Br, I, NCS; M = Cu, X = Cl, Br; M = Zn, X = Cl, Br, I, NCS$*; BBTE = 1,2-bis(2-benzothiazolyl)ethane),* $M(BMBE)X_2$ *(*$M = Co, X = Br, I; M = Cu, X = Cl$*; BMBE = 1,2-bis(2′-benzimidazolyl-5′-methyl)ethane),* $M(LP)X_2$ *(*$M = Cu, X = Cl; M = Zn, X = Cl, Br, I, NCS, NO_3$*),* $Cu(LP)_2(ClO_4)_2$ *(LP = 1,2-bis(2′-imidazolin-2′-yl)benzene). The four-coordinate cobalt complexes have distorted tetrahedral structures, while for the copper systems stereochemistries closer to square planar are apparent. The zinc complexes are pseudo tetrahedral with the exception of the complex* $Zn(LP)(NO_3)_2$ *which is six-coordinate. The benzothiazole ligand functions as a nitrogen donor and although all ligating groups are imidazole-like the imidazoline system is the strongest ligand. The bridging entity between the two donor groups also appears to influence ligand field strength (Dq BBTE* $\leqslant$ *BMBE* $<$ *LP).*

Introduction

Histidine imidazole is found at the active sites of numerous metalloprotein and metalloenzyme systems, *e.g.* the Type 1 copper centres in such enzymes as plastocyanin [1] and azurin [2] contain imidazole as well as sulphur donor groups. We have investigated a number of bidentate pseudo-imidazole ligands in which the donor groups have included benzothiazoles and imidazolines (Fig. 1). Nickel(II), cobalt(II), copper(II) and zinc(II) complexes of OBT, 1,2-bis(2-benzothiazolyl)benzene, cobalt(II) and nickel(II) complexes of LP, 1,2-bis(2′-imidazolin-2′-yl)benzene, and nickel(II) complexes of BBTE, 1,2-bis(2-benzothiazolyl)ethane, have been reported [3–5]. Also the nickel(II), cobalt(II) and copper(II) coordination chemistry of some tetradentate, 'tripod', ligands involving benzimidazole and benzothiazole functional groups has been published [6–10]. In all cases involving benzothiazole functional groups the ligands behave as nitrogen donors.

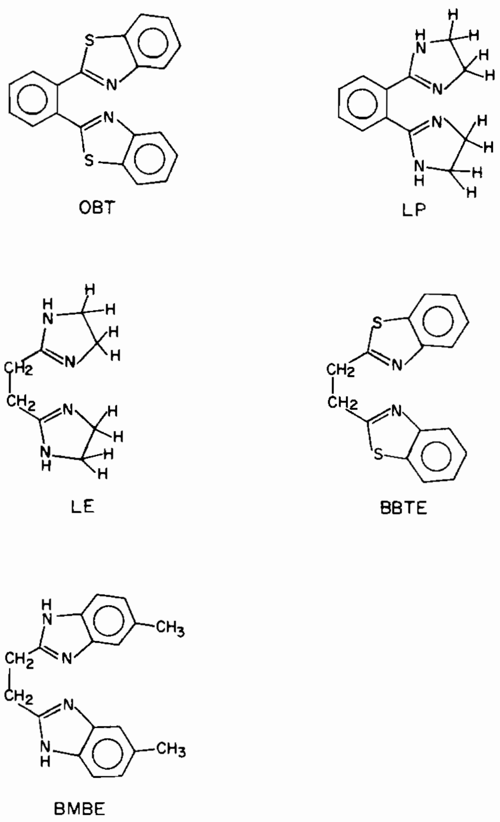

Fig. 1.

Copper complexes of the bidentate pseudoimidazole ligand OBT exhibit close to square or pseudo-octahedral geometries with little tendency toward tetrahedral coordination, typical of the Type 1

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TABLE I. Analytical Data.

	Compound	Colour	Found (%)				Calcd (%)			
			C	H	N	M	C	H	N	M
I	Co(BBTE)Cl_2	Blue	45.0	2.54	6.52	13.5	45.1	2.84	6.57	13.8
II	Co(BBTE)Br_2	Blue	37.5	2.01	5.35	11.1	37.3	2.35	5.44	11.5
III	Co(BBTE)I_2·½EtOH	Green	32.0	1.83	4.36	9.63	32.3	2.37	4.59	9.33
IV	Co(BBTE)$(NCS)_2$	Blue	45.7	2.40	11.2	12.1	45.9	2.57	11.9	12.5
V	Cu(BBTE)Cl_2	Khaki	44.3	2.62	6.32	14.8	44.6	2.81	6.50	14.8
VI	Cu(BBTE)Br_2	Khaki-brown	36.9	1.92	5.26	12.3	37.0	2.30	5.39	12.2
VII	Zn(BBTE)Cl_2	Light yellow	44.2	2.57	6.33	14.9	44.4	2.77	6.47	15.1
VIII	Zn(BBTE)Br_2	Yellow	37.0	2.08	5.24	12.3	36.8	2.30	5.37	12.5
IX	Zn(BBTE)I_2	Yellow	31.3	1.66	4.46	10.3	31.2	1.95	4.55	10.6
X	Zn(BBTE)$(NCS)_2$	Yellow	45.2	2.25	11.2	13.5	45.2	2.51	11.7	13.7
XI	Co(BMBE)Br_2	Blue	42.2	3.52	10.5	11.2	42.5	3.60	11.0	11.6
XII	Co(BMBE)I_2	Green	36.1	3.29	8.97	9.50	35.8	3.00	9.30	9.78
XIII	Cu(BMBE)Cl_2·½H_2O	Green	49.8	4.14	12.9	14.8	49.8	4.38	12.9	14.6
XIV	Cu(LP)Cl_2	Green	41.3	3.91	15.7	18.0	41.3	4.02	16.1	18.2
XV	$Cu(LP)_2(ClO_4)_2$	Khaki	41.5	4.23	15.9	9.20	41.7	4.06	16.2	9.20
XVI	Zn(LP)Cl_2	White	41.2	3.77	15.8	18.5	41.1	3.99	15.9	18.7
XVII	Zn(LP)Br_2	White	33.1	2.82	12.4	15.0	32.8	3.18	12.7	14.9
XVIII	Zn(LP)I_2	White	27.2	2.43	10.3	12.0	27.0	2.62	10.5	12.3
XIX	Zn(LP)$(NCS)_2$·EtOH	White	43.2	4.23	19.2	14.5	43.5	4.53	19.0	14.8
XX	Zn(LP)$(NO_3)_2$·½H_2O	White	35.2	3.41	20.4	15.7	34.9	3.64	20.4	15.9

centres. The complex Cu(OBT)Cl_2 has been shown to have an almost planar structure with a dihedral angle of 9.8° [11]. The 'tripod' ligands form predominantly five-coordinated trigonal bipyramidal copper(II) derivatives and some six-coordinate complexes (7, 9, 10). Here the five-coordinate geometries appear to have resulted from the steric constraints imposed by the ligands themselves. The inherent aversion of copper(II) centres to regular cubic geometries will, of necessity, prevent most simple bidentate and multidentate ligands from presenting the metal centre with a tetrahedral bite, unless unusual steric constraints are involved.

In this study we describe the synthesis and characterization of a number of cobalt(II), copper(II), and zinc(II) complexes of the bidentate pseudoimidazole ligands BBTE, LP and BMBE, 1,2-bis-(2'-benzimidazolyl-5'-methyl)ethane (Fig. 1). In the cases of the copper(II) complexes close to square planar geometries are indicated on the basis of spectroscopic evidence.

Experimental

The ligands LP [3], BBTE [12] and BMBE [13] were synthesized according to published procedures.

Co(BBTE)Cl_2 (I)

$CoCl_2·6H_2O$ (1.0 g; 4.2 mmol) was dissolved in hot ethanol (50 ml) and TEOF (triethylorthoformate) (10 ml) added. BBTE (0.50 g; 17 mmol) was dissolved in a minimum volume of hot ethanol and the solutions mixed. A blue crystalline product formed almost immediately. The reaction mixture was cooled and the product filtered, washed with ethanol and petroleum ether and dried under vacuum at 80 °C for 3 h (yield 0.53 g).

Complexes II–X were prepared in a similar fashion using an excess of metal salt in ethanol/TEOF. In some cases prolonged heating and reduction in volume of the solution were necessary to induce crystallization of the product.

Complexes XI–XX, involving the ligands BMBE and LP, were prepared by the same general procedure using ethanol/TEOF as solvent. The products were obtained for the most part as crystalline solids and used without further purification (Table I).

Physical Measurements

Electronic spectra were recorded with a Cary 17 spectrometer and infrared spectra with a Perkin-Elmer model 283 spectrometer. Magnetic susceptibilities were obtained at room temperature by the Faraday method using a Cahn Model #7600 Faraday

Magnetic Susceptibility system, coupled to a Cahn gram electrobalance. Electron spin resonance spectra (frozen solution, 77 K) were recorded on a Varian E-3 spectrometer at X-band frequency. (Magnetic field strengths were calibrated with an NMR probe and with Mn(II) in MgO powder.) Nuclear magnetic resonance data were obtained in deuterated DMSO with Varian Associates EM360 and Brüker WP-80 spectrometers using $SiMe_4$ as internal calibrant. Microanalyses were carried out by Canadian Microanalytical Service, Vancouver (C, H, N). Metal analyses were determined by atomic absorption with a Varian Techtron AA-5, after digestion of the samples in concentrated HNO_3 or aqua regia.

Results and Discussion

Ligand Field Spectra and Structure

The cobalt(II) complexes, which are all blue or green in colour, exhibit typical pseudo tetrahedral absorptions with three components visible in both the ν_2 and ν_3 transition envelope (the lower energy ν_1 absorption was not observed). The splitting of these bands is indicative of symmetries lower than tetrahedral, which would be expected for a system with a CoN_2X_2 chromophore. Values of 10 *Dq*, computed by estimating the centre of gravity of the ν_2 and ν_3 transitions and using the transition energy ratio method [14] are internally self consistent with *Dq*, I < Br < Cl < NCS for the ligand BBTE. The cobalt chloride and thiocyanate complexes of the ligand BMBE were synthesized but could not be obtained in an analytically pure state and so are not reported. However a comparison of the bromo- and iodo- complexes of the two ligands indicates that BBTE and BMBE are at least comparable in terms of their ligand field strength. This is reasonable assuming that the benzothiazole ligand, BBTE, involves nitrogen rather than sulphur donation. The obviously distorted nature of these complexes and the lack of structural data renders a more sophisticated discussion of their spectra somewhat futile.

While the ligand field strengths of the benzothiazole ligand, BBTE, and the benzimidazole ligand, BMBE, are comparable, a comparison with the other bidentate pseudo-imidazole ligand systems (OBT, LP, LE; Fig. 1) reveals two important points; (*1*) the imidazoline group is a stronger ligand than benzimidazole and benzothiazole and is more comparable with imidazole itself [3–5, 15] and (*2*) the bridging entity between the two donor groups is an important factor in determining ligand field strength. In a comparison of *e.g.* the bromo-complexes, $CoLBr_2$, the following ordering in terms of *Dq* was observed; OBT < BBTE ≤ BMBE < LP < LE. The enhancement of the ligand field strength on replacement of an *o*-phenylene bridge by an ethylene bridge can be seen as a result of the increased size of the ethylene bridge and its greater flexibility which could possibly allow more efficient ligand binding to the cobalt(II) centres.

Although no structural data are available for the cobalt complexes under discussion the X-ray structure of the complex $Ni(BBTE)Br_2$ has been reported [16] and indicates a distorted tetrahedral coordination about the nickel(II) centre with a dihedral angle between the Br–Ni–Br and N–Ni–N planes of 87.7°. The Br–Ni–Br angle is 131.8° and the N–Ni–N angle 109.6°; the other angles are compressed accordingly.

The ligand field spectra of the copper(II) complexes of BBTE, BMBE and LP are characterized by having a broad absorption in the range 14000–16000 cm^{-1} with, in some cases, a second band around 20000 cm^{-1} (Table II). Copper(II) complexes of the ligand OBT have been reported [4] and exhibit comparable spectra. An X-ray structure of the derivative $Cu(OBT)Cl_2$ [4, 11] reveals a distorted square planar structure with a dihedral angle of 9.8°. Similar structures are expected for the copper chloride and bromide complexes of the ligands BBTE, BMBE and LP. In the case of the complex $Cu(LP)_2(ClO_4)_2$ (XV), which appears to be similar to the complex $Cu(OBT)_2(ClO_4)_2$ [4], a near square planar, CuN_4 structure is anticipated. Systems of this sort usually exhibit two major absorptions with the higher energy band appearing above 20000 cm^{-1}. $Cu(L)_2(ClO_4)_2$, (L = 1,2-bis(2′-pyridyl)ethane), which is assumed to have a square planar structure, has absorptions at 18200 and 21600 cm^{-1} [17].

Magnetism and ESR Spectra

Magnetic moments (Table II) for the cobalt(II) derivatives fall in the range 4.33–4.65 B.M. typical of tetrahedral cobalt(II) systems of this type, while those of the copper(II) derivatives are normal.

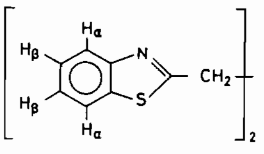
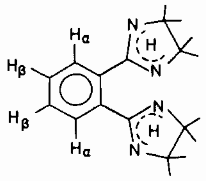
The frozen (77 K) nitromethane glass ESR spectrum of one complex $Cu(LP)_2(ClO_4)_2$ (XV) is typical of an axial species with $g_\parallel = 2.219$, $g_\perp = 2.044$, $|A_\parallel| = 160 \times 10^{-4}$ cm^{-1} and $|A_\perp| = 47 \times 10^{-4}$ cm^{-1}. It has been observed that values of $g_\parallel$ and $|A_\parallel|$ reflect the extent of tetrahedral distortion in CuN_4 systems and that straight line plots of $g_\parallel$ *versus* $|A_\parallel|$ are obtained for copper(II) complexes of pyrrole-2-carboxaldimines [18], dipyrromethenes [19] and salicylaldimines [20]. In the case of the pyrrole-2-carboxaldimines [18] the complex Cu(P2A-H)$_2$ is essentially planar [21] while with a large bulky substituent bound to the amine nitrogen in Cu(P2A-^{t}Bu)$_2$ a pseudo-tetrahedral coordination geometry is observed [22] with a dihedral angle of about 60°. Assuming that no significant change in geometry occurs in solution in toluene (the spectral solvent) at 77 K, the plot of $g_\parallel$ *versus*

TABLE II. Infrared Spectra, Magnetic Moments and Electronic (Mull Transmittance) Spectra.

	Compound	Infrared (cm^{-1})	μ (BM)[a]	d–d (cm^{-1})[b]	10 Dq (cm^{-1})	B (cm^{-1})	β
I	$Co(BBTE)Cl_2$	313, 333 νCoCl	4.33	6300, 7500, 9200 ν_2 15600, 16400, 17400 ν_3	4340	723	0.74
II	$Co(BBTE)Br_2$	257, 262, νCoBr	4.46	6200, [6800], 9200 ν_2 15400, 16000, 16900 ν_3	4330	699	0.72
III	$Co(BBTE)I_2 \cdot ½EtOH$		4.65	[6000], 6500, 8800 ν_2 14700, 15200, 16100 ν_3	4180	670	0.69
IV	$Co(BBTE)(NCS)_2$	295, 325, νCoNCS 2020, 2040sh νCN	4.37	[7700], 8500, [9500] ν_2 16500, 16900, 17700 ν_3	5060	693	0.71
XI	$Co(BMBE)Br_2$	250 νCoBr	4.43	6300, 7500, 9000 ν_2 15500, 16000, 16800 ν_3	4380	700	0.72
XII	$Co(BMBE)I_2$		4.58	6060, 7100, 8600 ν_2 14700, 15400, 16300 ν_3	4280	659	0.68
V	$Cu(BBTE)Cl_2$	332 νCuCl	2.03	14800, 19600			
VI	$Cu(BBTE)Br_2$	238sh, 243 νCuBr	1.76	[14000], 16000			
VIII	$Cu(BMBE)Cl_2 \cdot ½H_2O$	330 νCuCl	2.03	14200			
XIV	$Cu(LP)Cl_2$	300, 323, νCuCl	1.79	15500			
XV	$Cu(LP)_2(ClO_4)_2$	1080sh, 1100(ClO_4^-)	1.77	16100, 20800			
VII	$Zn(BBTE)Cl_2$	300, 320 νZnCl; 230, 240 νZnN					
VIII	$Zn(BBTE)Br_2$	240 νZnBr					
IX	$Zn(BBTE)I_2$	235 νZnN					
X	$Zn(BBTE)(NCS)_2$	290, 310 νZnNCS; 245 νZnN; 2040, 2090 νCN(NCS)					
XVI	$Zn(LP)Cl_2$	275, 290 νZnCl					
XVII	$Zn(LP)Br_2$	220, 235 νZnBr					
XIX	$Zn(LP)(NCS)_2 \cdot EtOH$	260, 280 νZnNCS, 2060, 2080sh, νCN(NCS)					
XX	$Zn(LP)(NO_3)_2 \cdot ½H_2O$	265, 275 νZnNO$_3$; 1720, 1756 ($\nu_1 + \nu_4$)NO$_3$					

[a] Magnetic moment measured in the solid state by the Faraday method (room temperature). [b] Electronic transitions for cobalt(II) complexes $\nu_2(^4T_1 \leftarrow {}^4A_2)$, $\nu_3(^4T_1(P) \leftarrow {}^4A_2)$. [ ] = shoulder.

TABLE III. Nuclear Magnetic Resonance Data (ppm in DMSO-d_6).[a]

	Compound	δH_α (m)	δH_β (m)	δCH_2 (s)		
	BBTE	7.95	7.40	3.71		
VII	Zn(BBTE)Cl_2	7.98	7.43	3.71		
VIII	Zn(BBTE)Br_2	7.96	7.41	3.73		
IX	Zn(BBTE)I_2	7.99	7.44	3.71		
X	Zn(BBTE)$(NCS)_2$	7.96	7.41	3.72		
		δH_α (AA'BB')	δH_β	δCH_2 (s)	δNH (s)	
	LP	7.53	7.46	3.54	6.85	
XVI	Zn(LP)Cl_2	7.63s	7.63s	3.62, 3.72, 3.82, 3.91q	8.34	
XVII	Zn(LP)Br_2	7.63s	7.63s	3.63, 3.72 3.82, 3.92q	8.43	
XVIII	Zn(LP)I_2	7.71s	7.71s	3.68, 3.78 3.85, 3.95q	8.70, 8.84	
XIX	Zn(LP)$(NCS)_2$•EtOH	7.68s	7.68s	3.70, 3.75 3.80, 3.85q	8.65	
XX	Zn(LP)$(NO_3)_2$•½H_2O	7.70s	7.70s	3.65	8.82	

[a] m = multiplet, s = singlet, q = quartet.

$|A_\parallel|$ may be of value in estimating the extent of distortion in other CuN_4 systems. The ESR parameters for XV fall directly on the plot of $g_\parallel$ *versus* $|A_\parallel|$ for the pyrrole-2-carboxaldimines described by Addison *et al.* [18] midway between the two cases quoted above. While it is perhaps tempting to approximate the degree of distortion in XV, based on values of $g_\parallel$ and $|A_\parallel|$, clearly the most that can be said is that this system is likely to be somewhat tetrahedrally distorted in the frozen glass.

Frozen glass spectra for the other copper complexes were not recorded because of their lack of solubility in suitable solvents.

Infrared and NMR Spectra

Infrared absorptions associated with cobalt–halogen, copper–halogen and zinc–halogen bonds were identified and are listed in Table II. Metal–nitrogen (ligand) absorptions have been assigned for several zinc complexes only while metal–nitrogen (thiocyanate) absorptions have been assigned for complexes IV, X and XIX. Two CN stretching frequencies associated with the coordinated thiocyanate groups are found in each case in the range 2020–2090 cm^{-1} consistent with terminal, nitrogen bound thiocyanate, in pseudo tetrahedral structures. The metal chloride and bromide complexes are characterized by having up to two metal–halogen bands consistent with C_{2v} local site symmetries. In those cases where spectral resolution in this region was poor and only one band was observed the same structural conclusions are assumed to be valid. Metal–iodide vibrations were not observed.

The complex XV exhibits a broad absorption at 1100 cm^{-1} with little fine structure, indicating ionic perchlorate and consistent with the four coordinate structural assignment for this system. Compound XX exhibits two nitrate combination $(\nu_1 + \nu_4)$ bands at 1720 and 1756 cm^{-1}, which are assigned to bidentate nitrate [23]. This complex therefore appears to have a six-coordinate solid state structure.

The NMR spectrum of the ligand BBTE in DMSO-d_6 (Table III) consists of a singlet at 3.71 ppm, associated with equivalent methylene groups, and two unsymmetrical multiplets at 7.40 ppm and 7.95 ppm due to the *alpha* and *beta* protons respectively on the fused benzene ring. The lack of symmetry associated with these aromatic protons results from the asymmetric nature of the fused thiazole ring, in sharp contrast to symmetrically *o*-disubstituted benzene rings and 2-substituted benzimidazoles [6], in which typical AA'BB' splitting patterns are observed. The NMR spectra of the zinc complexes of BBTE are almost identical with that of the free ligand with very small differences in the chemical shifts of the aromatic and aliphatic proton resonances. The most likely conclusion to draw here is that the solvent has displaced the ligand at the metal centre. This is substantiated by examining the UV spectra of the ligand and the zinc complexes VII–X in dimethylsulfoxide. Sharp intense bands founds at 34250 cm^{-1} and 35200 cm^{-1} for BBTE alone occur at exactly the same energy for all the complexes.

The ligand LP is characterized by an NMR spectrum exhibiting a singlet at 3.54 ppm due to equivalent methylene protons and a symmetric AA′-BB′ set of resonances at lower field associated with the α and β protons on the benzene ring, implying a plane of symmetry at right angles to the benzene ring and bisecting the molecule. A broad resonance at 6.85 ppm is assigned to NH, which is presumably associated equally with the two nitrogen atoms in the delocalised N–C–N framework of the imidazoline ring. Downfield shifts are observed for all resonances of the complexes implying that decomplexation has not occurred in solution in dimethylsulfoxide. The largest downfield shift was observed for the NH resonance with a fairly sharp singlet occurring in the range 8.30–8.90 ppm for all complexes except the iodide, XVIII, where two resonances attributable to NH were found. Identification of this as the NH resonance was confirmed by addition of D_2O to the NMR samples whereupon this resonance disappeared.

For all the complexes the aromatic resonances coalesce to form a single, fairly sharp absorption. The methylene resonance occurs as a broad singlet for the nitrate complex, XX, while for all others a quartet of peaks is observed (Table III). Resolution of the quartet is poor in most cases although for compounds XVI, XVII and XIX it is symmetric. For the iodo-complex (XVIII) it is very asymmetric. A quartet would not be expected and this set of resonances can be interpreted in terms of two overlapping triplets due to non-equivalent methylene groups. The spectrum of the iodo-complex is complicated further by the appearance of two NH resonances indicating slightly non-equivalent imidazoline rings. This may be responsible for the asymmetry associated with the methylene resonances.

The broad singlet methylene resonance of the nitrate complex is presumably associated with methylene groups that are essentially equivalent. This cannot be the result of symmetry within the imidazoline ring, because the NH resonance shifts downfield considerably on complexation, but is more likely the result of molecular motion within the ring itself. The non-equivalence of the methylene protons in the other complexes may be the result of a more rigid imidazoline ring system.

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