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Synthesis and Spectroscopic Studies of Metal Complexes of N,N′-p-Phenylenedimethylenebis(pyridin-4-one) with d- and f-Block Metal Ions

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SYNTHESIS AND REACTIVITY IN INORGANIC AND METAL-ORGANIC CHEMISTRY
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Synthesis and Spectroscopic Studies of Metal Complexes of *N*,*N*′-*p*-Phenylenedimethylenebis(pyridin-4-one) with d- and f-Block Metal Ions

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ABSTRACT

The preparations are reported for a range of complexes of the ligand *N*,*N*′-*p*-phenylenedimethylene*bis*(pyridin-4-one) (XBP) with the d-block ions Mn(II) to Zn(II) and also with Cd(II), Y(III), and the lanthanide ions. Relevant solid state EPR, electronic and far-IR spectra are reported and interpreted in terms of the metal ion coordination geometries and, where appropriate, the likely long-range polymeric structures of the compounds. The value of the zero-field splitting (zfs) parameter, $D = 0.069\,\mathrm{cm}^{-1}$, obtained from the $S = 1$ type EPR spectrum of the compound $\{[Cu_2(XBP)_3(NO_3)_2](NO_3)_2 \cdot 2H_2O\}_n$ is compared with those of other compounds involving discrete $Cu \cdots Cu$ dimer interaction. The results

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of luminescence measurements on the complexes of Sm(III), Eu(III), Tb(III), and Dy(III) are also given.

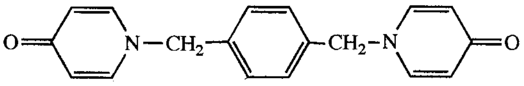
Key Words: Polymeric complexes; Transition metals; Lanthanides; EPR; Electronic spectra; Luminescence spectra.

INTRODUCTION

The synthesis of new polymeric metal complexes forming either sheet structures involving contiguous arrays of large metallacyclic rings or three-dimensional networks continues to attract attention because of their potential as metal-organic analogues of zeolites. Several variables can be employed in design strategies for materials of this type. A wide range of metal ions can be used as "node" points in such compounds, often with attendant variations in metal ion coordination geometry. Additionally, the types of donor groups coordinated to the metal centres by the organic bridging ligands can be varied, as can the lengths and geometries of the "spacer" unit connecting those donor groups. In such solid state materials further factors such as hydrogen bonding and $\pi-\pi$ stacking interactions may often play an appreciable role in influencing the type of structure that results.[1,2]

The great majority of the organic bridging ligands used in this area of research contains nitrogen donor groups, such as pyridine units, and many different structural types have been reported.[1,3–12] Those with O-donor groups have received rather less attention,[1] although work involving carboxylate anions as bridging ligands is producing an increasing range of interesting structures.[13–19]

We have previously shown that neutral O-donor "extended reach" ligands containing pyridone units as donor end-groups readily form coordination polymers with both transition metal[20] and lanthanide[21] ions. As x-ray studies showed that the ligand *N*,*N*′-*p*-phenylenedimethylene*bis*(pyridin-4-one) (XBP) (Fig. 1) formed several polymeric complexes with particularly complex, interwoven structures[22–24] we have explored the synthesis and spectroscopic properties of a wider range of compounds formed by XBP and we report here the results of that work.



XBP

Figure 1. Formula of XBP.

RESULTS AND DISCUSSION

The complexes of XBP we have obtained are listed in Tables 1 and 2 for some d- and f-block metal ions, respectively.

Complexes of Mn(II) to Zn(II) and Cd(II)

All the cobalt(II) complexes are of the type $Co(XBP)X_2$, where $X = NO_3$, Cl, Br, I, or NCS, but their solid state electronic spectra clearly show that the coordination geometry at the cobalt centre is anion-dependent. The bright blue complexes formed by cobalt(II) halides and cobalt(II) isothiocyanate all show the characteristic, strong, three-component d–d bands (Fig. 2, band energies listed in Table 3) arising from the transitions ν_2 [$^4A_2(F) \rightarrow {}^4T_1(F)$ in the near-IR region] and ν_3 [$^4A_2(F) \rightarrow {}^4T_1(P)$ centred on *ca* 16,000 cm^{-1}], expected for an essentially tetrahedral CoO_2X_2 chromophore of C_{2v} symmetry.[25] In the case of the cobalt(II) chloride complex additional evidence for the pseudotetrahedral geometry at the cobalt centre[26] is provided by the presence of $\nu_{as}(Co{-}Cl)$ and $\nu_{sym}(Co{-}Cl)$ bands at 318 and 289 cm^{-1}, respectively, in its far-IR vibrational spectrum. The analogous complex of zinc(II) chloride has a similar pair of $\nu(Zn{-}Cl)$ vibrational bands at 316 and 281 cm^{-1} respectively, again consistent with a distorted tetrahedral, C_{2v}, coordination geometry. Although crystals of sufficient quality for single crystal x-ray study were not obtained for these compounds, it seems likely that their long-range structures take the form of polymeric chains in which the tetrahedrally coordinated metal centres are linked by the XBP ligands.

In contrast, the electronic spectrum (Table 3) of the purple complex formed by cobalt(II) nitrate is characteristic of an essentially octahedral CoO_6 chromophore.[27] In view of the 1 : 1 XBP : Co stoichiometry, the six-coordination would be achieved either by the presence of bidentate anions at each cobalt centre in a $[Co(XBP)(NO_3)_2]_n$ chain or a more complex array structure involving both XBP and nitrate bridges between the metal atoms.

The electronic spectra of the nickel(II) complexes $Ni(XBP)Cl_2 \cdot H_2O$ and $Ni(XBP)_2(ClO_4)_2 \cdot 2H_2O$ (Table 3) also show the presence of essentially octahedral coordination geometry at the metal centres as the d–d bands are of relatively low intensity and at energies expected[28] for the transitions ν_1 [$^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$] and ν_2 [$^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$]. In each case, the band arising from ν_3[$^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$] is obscured by a very intense charge-transfer band at *ca.* 25,000 cm^{-1}. In view of the very poor coordinating ability of the perchlorate anion, the octahedral coordination observed for the nickel(II) perchlorate complex suggests that a possible long-range solid state structure is a sheet polymer formed by XBP bridges between the nickel

Table 1. Colours and analytical Results for some complexes of Mn(II), Co(II), Ni(II), Cu(II), Zn(II), and Cd(II) with XBP.

Complex	Colour	Formula weight	Yield (%)	Anal. found % (calcd. %) C	H	N
$[Mn(XBP)(NO_3)_2] \cdot 2H_2O$	Yellow	507	71	42.9	3.9	10.9
$C_{18}H_{20}MnN_4O_{10}$				(42.6)	(4.0)	(11.0)
$[Mn(XBP)Cl_2] \cdot 2.5H_2O$	Cream	463	64	46.7	4.7	6.0
$C_{18}H_{21}Cl_2MnN_2O_{4.5}$				(46.7)	(4.6)	(6.1)
$[Mn(XBP)Br_2] \cdot H_2O$	Cream	525	100	41.3	4.0	5.0
$C_{18}H_{18}Br_2MnN_2O_3$				(41.2)	(3.5)	(5.3)
$Mn(XBP)_2(ClO_4)_2 \cdot 3H_2O$	Yellow	893	54	48.4	3.9	6.2
$C_{36}H_{38}Cl_2MnN_4O_{15}$				(48.4)	(4.3)	(6.3)
$[Co(XBP)(NO_3)_2]$	Purple	475	74	45.9	3.4	11.8
$C_{18}H_{16}CoN_4O_8$				(45.5)	(3.4)	(11.8)
$[Co(XBP)Cl_2] \cdot H_2O$	Blue	440	96	48.8	4.0	6.4
$C_{18}H_{18}Cl_2CoN_2O_3$				(49.1)	(4.1)	(6.4)
$[Co(XBP)Br_2]$	Blue	511	100	41.9	3.0	5.3
$C_{18}H_{16}Br_2CoN_2O_2$				(42.3)	(3.2)	(5.5)
$[Co(XBP)I_2]$	Blue	605	32	36.2	2.7	5.0
$C_{18}H_{16}CoI_2N_2O_2$				(35.7)	(2.7)	(4.6)

$[Co(XBP)(NCS)_2] \cdot 0.5H_2O$	Blue	476	65	50.8	3.6	11.3
$C_{20}H_{17}CoN_4O_{2.5}S_2$				(50.4)	(3.6)	(11.8)
$Ni(XBP)Cl_2 \cdot H_2O$	Blue-green	440	100	48.7	4.5	6.0
$C_{18}H_{18}Cl_2N_2NiO_3$				(49.1)	(4.1)	(6.4)
$Ni(XBP)_2(ClO_4)_2 \cdot 2H_2O$	Pale green	878	32	49.1	3.9	6.4
$C_{36}H_{36}Cl_2N_4NiO_{14}$				(49.2)	(4.1)	(6.4)
$Cu(XBP)Cl_2 \cdot 2.5H_2O$	Green-yellow	472	30	45.3	3.8	5.9
$C_{18}H_{21}Cl_2CuN_2O_{4.5}$				(45.8)	(4.5)	(5.9)
$Cu(XBP)Br_2 \cdot 1.5H_2O$	Dark grey	543	71	39.7	3.2	5.1
$C_{18}H_{19}Br_2CuN_2O_{3.5}$				(39.8)	(3.5)	(5.2)
$Cu_2(XBP)_3(NO_3)_4 \cdot 2H_2O$	Green	1,288	70	49.9	4.3	10.6
$C_{54}H_{52}Cu_2N_{10}O_{20}$				(50.4)	(4.1)	(10.9)
$Zn_2(XBP)_3(NO_3)_4 \cdot 4H_2O$	Cream	1,328	84	49.0	3.8	10.4
$C_{54}H_{56}N_{10}O_{22}Zn_2$				(48.9)	(4.3)	(10.6)
$Zn(XBP)Cl_2 \cdot H_2O$	Cream	447	47	48.0	4.6	6.2
$C_{18}H_{18}Cl_2N_2O_3Zn$				(48.4)	(4.1)	(6.3)
$[Zn(XBP)I_2]$	Yellow	612	73	35.6	2.7	4.8
$C_{18}H_{16}I_2N_2O_2Zn$				(35.4)	(2.6)	(4.6)
$Zn(XBP)_2(ClO_4)_2 \cdot 2H_2O$	White	885	63	48.9	3.9	6.4
$C_{36}H_{36}Cl_2N_4O_{14}Zn$				(48.9)	(4.1)	(6.3)
$Cd(XBP)_3(ClO_4)_2 \cdot 2MeCN \cdot 2H_2O$	Yellow	1,306	74	53.5	4.2	8.6
$C_{58}H_{58}CdCl_2N_8O_{16}$				(53.3)	(4.5)	(8.6)

Table 2. Colours and analytical Results for some complexes of XBP with lanthanide(III) ions and with Y(III) perchlorate.

Complex	Colour	Formula weight	Yield (%)	Anal. found % (calcd. %) C	H	N
$La_4(XBP)_7(NO_3)_{12} \cdot 4H_2O$	Cream	3,418	64	44.7	3.3	10.4
$C_{126}H_{120}La_4N_{26}O_{54}$				(44.3)	(3.5)	(10.7)
$Ce_4(XBP)_7(NO_3)_{12} \cdot 4H_2O$	Pale yellow	3,423	65	44.6	3.4	10.6
$C_{126}H_{120}Ce_4N_{26}O_{54}$				(44.2)	(3.5)	(10.6)
$Pr_4(XBP)_7(NO_3)_{12} \cdot 4H_2O$	Pale green	3,426	73	44.2	3.4	10.5
$C_{126}H_{120}N_{26}O_{54}Pr_4$				(44.2)	(3.5)	(10.6)
$Nd_4(XBP)_7(NO_3)_{12} \cdot 4H_2O$	Pale mauve	3,439	73	43.8	3.2	10.4
$C_{126}H_{120}N_{26}Nd_4O_{54}$				(44.0)	(3.5)	(10.6)
$Sm_4(XBP)_7(NO_3)_{12} \cdot 4H_2O$	Pale yellow	3,464	73	43.9	3.2	10.5
$C_{126}H_{120}N_{26}Sm_4O_{54}$				(43.7)	(3.5)	(10.5)
$Eu_4(XBP)_7(NO_3)_{12} \cdot 4H_2O$	Pale yellow	3,470	63	44.1	3.2	10.4
$C_{126}H_{120}Eu_4N_{26}O_{54}$				(43.6)	(3.5)	(10.5)
$Gd_2(XBP)_3(NO_3)_6 \cdot 2H_2O$	Cream	1,600	84	40.8	3.1	10.4
$C_{54}H_{52}Gd_2N_{12}O_{26}$				(40.6)	(3.3)	(10.5)
$Tb_2(XBP)_3(NO_3)_6 \cdot 2H_2O$	Pale yellow	1,603	82	40.6	2.8	10.2
$C_{54}H_{52}N_{12}O_{26}Tb_2$				(40.5)	(3.3)	(10.5)
$Dy_2(XBP)_3(NO_3)_6 \cdot 2H_2O$	Yellow	1,610	73	40.1	3.1	10.1
$C_{54}H_{52}Dy_2N_{12}O_{26}$				(40.3)	(3.3)	(10.4)
$Ho_2(XBP)_3(NO_3)_6 \cdot 2H_2O$	Yellow	1,615	68	40.2	3.1	10.1
$C_{54}H_{52}Ho_2N_{12}O_{26}$				(40.2)	(3.3)	(10.4)
$Er_2(XBP)_3(NO_3)_6 \cdot 2H_2O$	Pink	1,620	74	40.2	3.0	10.1
$C_{54}H_{52}Er_2N_{12}O_{26}$				(40.1)	(3.2)	(10.4)

$Yb_2(XBP)_3(NO_3)_6 \cdot 2H_2O$	Cream	1,631	77	39.5	2.9	10.2
$C_{54}H_{52}N_{12}O_{26}Yb_2$				(39.8)	(3.2)	(10.3)
$Pr_2(XBP)_3Cl_6 \cdot 8H_2O$	Green	1,516	81	43.0	4.0	5.7
$C_{54}H_{64}Cl_6N_6O_{14}Pr_2$				(42.8)	(4.3)	(5.5)
$Nd_2(XBP)_3Cl_6 \cdot 8H_2O$	Mauve	1,522	80	42.4	4.4	5.6
$C_{54}H_{64}Cl_6N_6Nd_2O_{14}$				(42.6)	(4.2)	(5.5)
$Eu_2(XBP)_3Cl_6 \cdot 2H_2O$	Pale yellow	1,430	62	45.8	3.8	6.0
$C_{54}H_{52}Cl_6$ $Eu_2N_6O_8$				(45.4)	(3.7)	(5.9)
$Tb_2(XBP)_3Cl_6 \cdot 2H_2O$	Cream	1,444	100	44.6	4.1	5.7
$C_{54}H_{52}Cl_6N_6O_8Tb_2$				(44.9)	(3.6)	(5.8)
$Dy_2(XBP)_3Cl_6$	Yellow	1,415	100	46.4	3.8	6.0
$C_{54}H_{48}Cl_6Dy_2N_6O_6$				(45.9)	(3.4)	(5.9)
$Yb_2(XBP)_3Cl_6$	Cream	1,436	100	45.7	4.0	5.8
$C_{54}H_{48}Cl_6N_6O_6Yb_2$				(45.2)	(3.4)	(5.9)
$Y(XBP)_3(ClO_4)_3 \cdot 2H_2O$	Cream	1,300	100	49.7	4.1	6.4
$C_{54}H_{52}Cl_3N_6O_{20}Y$				(49.9)	(4.0)	(6.5)
$La_2(XBP)_7(ClO_4)_6 \cdot 7H_2O$	Pale yellow	3,047	100	49.8	4.2	6.4
$C_{126}H_{126}Cl_6La_2N_{14}O_{45}$				(49.7)	(4.2)	(6.4)
$Nd_2(XBP)_7(ClO_4)_6 \cdot 7H_2O$	Pale lilac	3,058	43	49.0	4.0	6.4
$C_{126}H_{126}Cl_6N_{14}Nd_2O_{45}$				(49.5)	(4.2)	(6.4)
$Sm_2(XBP)_7(ClO_4)_6 \cdot 4H_2O$	Yellow	3,016	99	50.2	4.1	6.5
$C_{126}H_{120}Cl_6N_{14}O_{42}Sm_2$				(50.2)	(4.0)	(6.5)
$Gd_2(XBP)_7(ClO_4)_6 \cdot 7H_2O$	Pale yellow	3,083	100	48.7	4.1	6.3
$C_{126}H_{126}Cl_6Gd_2N_{14}O_{45}$				(48.8)	(4.1)	(6.4)
$Dy(XBP)_3(ClO_4)_3 \cdot 2H_2O$	Cream	1,374	87	47.0	4.0	6.1
$C_{54}H_{52}Cl_3DyN_6O_{20}$				(47.2)	(3.8)	(6.1)

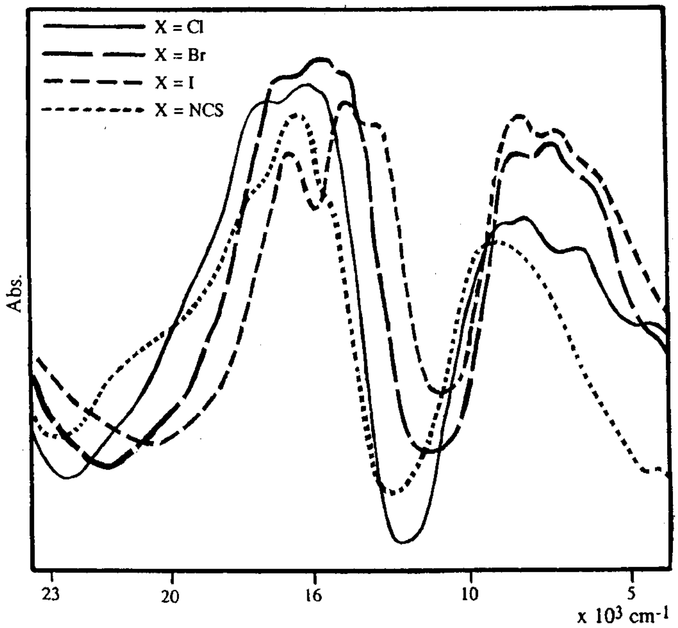


Figure 2. Electronic spectra of the solid complexes $Co(XBP)_2X_2$ (X = Cl, Br, I, and NCS).

centres, with pairs of aqua ligands in *trans*-positions. The compound may thus be formulated as $\{[Ni(XBP)_2(H_2O)_2](ClO_4)_2\}_n$. The long-range structure of the nickel(II) chloride complex is less clear but the stoichiometry suggests that the six-coordination is achieved by a combination of both XBP and chloride bridges, with possible aqua ligand bonding.

All the manganese(II) complexes have very simple X-band EPR spectra consisting of a single band at $g_{\mathrm{eff}} = 2.0$, with no evidence of any significant zero-field splitting (zfs). Spectra of this type are consistent with either a coordination geometry of very high symmetry at the manganese(II) centres or the presence of sufficiently strong dipolar coupling between those centres to cause the loss of the zfs.[29] The considerable distance between the pair of donor oxygen atoms in the XBP ligand renders it most unlikely that the linking of manganese(II) centres by such XBP bridges would result in sufficient magnetic interaction to cause the collapse of the multi-band structure indicative of zfs.

It is, however, a well-established feature of coordination chemistry that chloro- and bromo complexes of the type ML_2X_2 (where L = a unidentate donor ligand) frequently achieve six-coordination at the metal ion by the bridging action of the halide ions, and such bridges result in an efficient

Table 3. Electronic band energies (in cm^{-1}) for the cobalt(II), nickel(II), and copper(II) complexes of XBP in the solid state.

Compound	Electronic band energies[a]
$[Co(XBP)(NO_3)_2]$	8,000, 13,325, 17,200 sh, 18,500, 20,200 sh
$[Co(XBP)Cl_2] \cdot H_2O$	5,800, 7,100, 8,125 sh, 15,625 sh, 16,125, 17,400
$[Co(XBP)Br_2]$	5,575 sh, 6,325, 7,400 sh, 15,150 sh, 15,875, 17,100 sh
$[Co(XBP)I_2]$	5,400 sh, 6,175, 7,300, 14,400 sh, 15,275, 17,125
$[Co(XBP)(NCS)_2] \cdot 0.5H_2O$	8,250 br, 15,500 sh, 16,400, 17,800 sh
$Ni(XBP)Cl_2 \cdot H_2O$	8,200, 15,400
$Ni(XBP)_2(ClO_4)_2 \cdot 2H_2O$	8,850, 14,800
$Cu_2(XBP)_3(NO_3)_4 \cdot 2H_2O$	11,000 sh, 14,500
$Cu(XBP)Cl_2 \cdot 2.5H_2O$	5,700 sh, 12,050
$Cu(XBP)Br_2 \cdot 1.5H_2O$	5,550 sh, 11,350

[a] sh, shoulder and br, broad.

cause of the loss of zfs in the EPR spectrum when M = Mn(II).[29] Accordingly, the loss of the expected zfs in the manganese(II) chloride and bromide complexes of XBP is consistent with the presence of halide bridges between the metal centres. Further evidence for that is provided by their far-IR vibrational spectra, which have no $\nu(Mn-X)$ bands above 220 cm^{-1}. A decision as to whether, in each case, all the halide ions act as bridges between Mn centres or whether combinations of bridging and unidentate binding are present, as in the compound $[Mn(m\text{-}XBP)Cl_2]_n$ formed by the related ligand *N*,*N*′-*m*-phenylenedimethylene*bis*(pyridin-2-one),[30] would require a single-crystal x-ray study. An x-ray study would also elucidate the role of the water molecules in these compounds but crystals of sufficient quality were not obtained.

The single band EPR spectrum observed for the compound $Mn(XBP)_2(ClO_4)_2 \cdot 3H_2O$ suggests that it has the same type of long-range polymeric structure advanced for the nickel(II) perchlorate complex discussed previously and that it can be formulated as $\{[Mn(XBP)_2(H_2O)_2](ClO_4)_2 \cdot H_2O\}_n$.

The X-band EPR spectra of the copper(II) chloride and bromide complexes exhibit a single, very broad band at *ca.* $g = 2$, again indicating the presence of halide bridges resulting in extensive dipolar coupling between the copper(II) centres and loss of the resolution of g anisotropy.

The copper(II) nitrate complex of the stoichiometry $Cu_2(XBP)_3(NO_3)_4 \cdot 2H_2O$ has been previously shown[23] to have the formulation $\{[Cu_2(XBP)_3(NO_3)_2](NO_3)_2 \cdot 2H_2O\}_n$ and a structure in which pairs of copper atoms are linked by two μ–O(pyridone) bridges to form Cu_2O_2 units with a $Cu \cdots Cu$ separation of 3.34 Å and an $S = 1$ type EPR spectrum. That close $Cu \cdots Cu$ separation is depicted in Fig. 3 as a schematic drawing of the

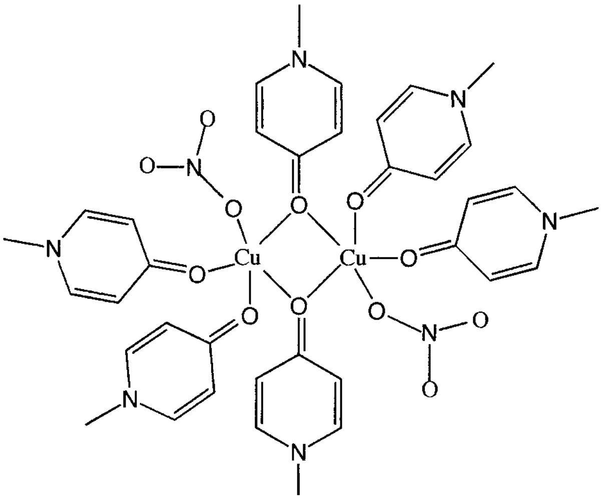


Figure 3. Schematic representation of the dinuclear [Cu_2O_2] unit in the structure of $\{[Cu_2(XBP)_3(NO_3)_2](NO_3)_2 \cdot 2H_2O\}_n$.

x-ray determined structure.[23] There is further extensive bridging action by the XBP ligands resulting in the formation of a complex, large-ring (68-membered), interwoven network of such units and a long-range structure which is best viewed by accessing it on the Cambridge Crystallographic Data Centre (compound ref. ZIGTAK).

Use of the equations given by Wasserman, Snyder, and Yager for the derivation of the g values and zfs parameters from the EPR spectra of randomly oriented $S = 1$ molecules[31] yields the values: $g_{xy} = 2.08$, $g_z = 2.21$, and $D = 0.069\,\mathrm{cm}^{-1}$. The zfs parameter, D, observed for this XBP complex of copper(II) nitrate is smaller than those found for some other antiferromagnetically coupled dimeric Cu(II) systems, such as copper(II) carboxylate dimers (D in range $0.3–0.45\,\mathrm{cm}^{-1}$)[32] or dimers formed by nitrogen donor bridges (e.g., adenine, hypoxanthine, 4-azabenzimidazole or 7-azaindole; D $0.1–0.18\,\mathrm{cm}^{-1}$)[33,34] or those employing both N- and O-donor ligands such as 3-ethyl-2-pyridone (for which $D = 0.29\,\mathrm{cm}^{-1}$).[35] A smaller D value would be expected from the larger Cu $\cdots$ Cu separation (3.34 Å) in $\{[Cu_2(XBP)_3(NO_3)_2](NO_3)_2 \cdot 2H_2O\}_n$ as compared with those in the dimers referred to above, for which Cu $\cdots$ Cu is in the range *ca.* 2.6–3.0 Å. Interestingly, an X-band EPR spectrum very similar to that of $\{[Cu_2(XBP)_3(NO_3)_2](NO_3)_2 \cdot 2H_2O\}_n$ has been reported[36] for the 1-methyluracil (1-MeU) complex *cis*-$[(NH_3)_2Pt(1\text{-}MeU)_2Cu(H_2O)_2]SO_4 \cdot 4.5H_2O$ in which pairs of *cis*-$[(NH_3)_2Pt(1\text{-}MeU)_2Cu(H_2O)_2]^{2+}$ cations pack in a centrosymmetric head–head arrangement with a Cu $\cdots$ Cu separation of 3.48 Å, but without any bridges between the two copper centres.[37]

Reaction of zinc(II) perchlorate with XBP gave the compound $Zn(XBP)_2(ClO_4)_2 \cdot 2H_2O$, whereas with zinc(II) nitrate the resulting complex was $Zn_2(XBP)_3(NO_3)_4 \cdot 4H_2O$. The 3 : 2 XBP : Zn stoichiometry observed for the latter compound suggests that it may have a structure similar to that found previously for the copper(II) nitrate complex.[23] The compound $\{[Zn_2(XBP)_4](BF_4)_4 \cdot 4H_2O\}_n$ is known[23] to contain closely similar M_2O_2 units (drawn schematically in Fig. 4; access Cambridge Crystallographic Data Centre, compound ref. ZIGSUD, to view full structure) but in which the coordinated nitrate groups present in the copper nitrate complex are each replaced by a coordinated pyridin-4-one unit in the zinc compound. It seems likely, therefore, that the zinc perchlorate complex is more appropriately formulated as $\{[Zn_2(XBP)_4](ClO_4)_4 \cdot 4H_2O\}_n$, with a structure in which XBP bridges generate a complex array of metallacyclic rings, with a combination of 34- and 38-membered rings, and with XBP "through-ring" threading,

The x-ray powder diffraction pattern of the complex of stiochiometry $Cd(XBP)_3(ClO_4)_2 \cdot 2MeCN \cdot 2H_2O$ shows that it is isostructural with the compound $Mn(XBP)_3(ClO_4)_2 \cdot 2MeCN$[22] and it has, therefore, the same polymeric structure involving polycatenated sheets of 34- and 68-membered rings with octahedral CdO_6 node points. It is appropriately formulated as $\{[Cd(XBP)_3](ClO_4)_2 \cdot 2MeCN \cdot 2H_2O\}_n$.

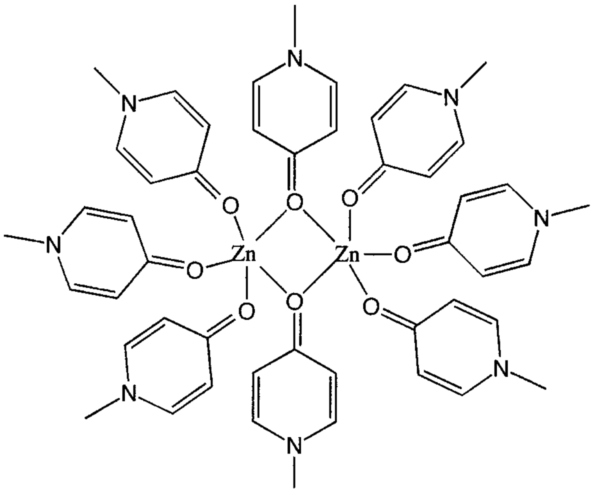


Figure 4. Schematic representation of the dinuclear $[Zn_2O_2]$ unit in the structure of $\{[Zn_2(XBP)_4](BF_4)_4 \cdot 4H_2O\}_n$.

Lanthanide Complexes

The stoichiometries of the complexes of XBP formed by the lanthanide(III) nitrates fall into two groups: those in the series La to Eu (Pm not studied) are of the type $M_4(XBP)_7(NO_3)_{12} \cdot 4H_2O$, whereas those from Gd to Yb have the stoichiometry $M_2(XBP)_3(NO_3)_6 \cdot 2H_2O$. A change in stoichiometry and/or structure in analogous complexes is frequently observed as one progresses across the lanthanide series (a manifestation of the discontinuity feature that is often found at gadolinium and which has been termed the "gadolinium break"[38]). It may be noted that reactions were also carried out with a representative member of each series (Nd and Er, respectively) varying the XBP : metal mole ratio (5 : 1, 2 : 1, and 1 : 5) and also the solvent medium employed (MeOH, EtOH, MeCN, and $MeNO_2$) but without any change in the stoichiometry or crystallinity of the resulting products. Unfortunately, we have been unable to obtain any member of either of the two series of lanthanide nitrate complexes in the form of x-ray-quality crystals for definitive structural analysis.

It also proved very difficult to obtain good quality crystals of members of the more limited ranges of lanthanide(III) chloride and perchlorate complexes listed in Table 2. The structure of one of them, $Nd_2(XBP)_7(ClO_4)_6 \cdot 7H_2O$, has been shown[24] to have the formula $\{[Nd_2(XBP)_6(H_2O)_4](XBP)(H_2O)_3(ClO_4)_6\}_n$ and to form a very complex array of chains of interpenetrating "cages" of 34-membered metallacycles with adjacent chains cross-linked by non-coordinated XBP molecules hydrogen-bonded to aqua ligands.

We have, however, taken the opportunity to explore the photoluminescence properties of a representative range of the Sm, Eu, Tb, and Dy complexes in the solid state (Table 4). The samarium complex $Sm_4(XBP)_7(NO_3)_{12} \cdot 4H_2O$ and the dysprosium complexes phosphoresce relatively weakly. The samarium

Table 4. Luminescence data for some lanthanide(III) complexes of XBP.

Compound	Excitation (nm)	Emission (nm)	Lifetime (μsec)
$Sm_4(XBP)_7(NO_3)_{12} \cdot 4H_2O$	377	563, 598, 643[a]	58
$Eu_4(XBP)_7(NO_3)_{12} \cdot 4H_2O$	396	593, 616[a]	613
$Tb_2(XBP)_3(NO_3)_6 \cdot 2H_2O$	346	490, 545[a], 583, 621	741
$Dy_2(XBP)_3(NO_3)_6 \cdot 2H_2O$	366	482, 575[a]	59
$Eu_2(XBP)_3Cl_6 \cdot 2H_2O$	395	593, 613[a]	359
$Tb_2(XBP)_3Cl_6 \cdot 2H_2O$	346	490, 547[a], 585, 621	624
$Dy(XBP)_3(ClO_4)_3 \cdot 2H_2O$	366	484, 576[a]	49

[a] Band used for lifetime measurements.

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complex exhibits low-intensity emission bands at 563 nm ($^4G_{5/2} \rightarrow {}^6H_{5/2}$), 598 nm ($^4G_{5/2} \rightarrow {}^6H_{7/2}$), and 643 nm ($^4G_{5/2} \rightarrow {}^6H_{9/2}$), whereas those for the dysprosium complexes are at *ca.* 483 nm ($^4F_{9/2} \rightarrow {}^6H_{15/2}$) and *ca.* 576 nm ($^4F_{9/2} \rightarrow {}^6H_{13/2}$). The europium complexes show strong phosphorescent emission, with bands at 593 nm ($^5D_0 \rightarrow {}^7F_1$) and *ca.* 615 nm ($^5D_0 \rightarrow {}^7F_2$). The terbium complexes luminesce very strongly and four dominant bands appear in their phosphorescence emission spectra at 490 nm ($^5D_4 \rightarrow {}^7F_6$), *ca.* 546 nm ($^5D_4 \rightarrow {}^7F_5$), *ca.* 584 nm ($^5D_4 \rightarrow {}^7F_4$), and 621 nm ($^5D_4 \rightarrow {}^7F_3$). The phosphorescence lifetimes (Table 4) are in the order $Tb^{3+} > Eu^{3+} \gg Sm^{3+} \approx Dy^{3+}$ and are similar in magnitude to those observed previously for polymeric complexes of these metal ions with *N,N′*-ethylene*bis*(pyrrolidin-2-one).[39] In view of the paucity of comparative data for such compounds with complex, interwoven, network structures further work on related compounds with well-documented structures is needed before further comments about these data are warranted.

EXPERIMENTAL

Synthesis

XBP

This was prepared as described previously.[22] The ligand crystallises as a tetrahydrate but is denoted below simply as XBP.

Metal Complexes of XBP

Caution! Although we did not observe any explosive behaviour with any of the perchlorate complexes described below, all metal perchlorates must be regarded as potentially explosive and appropriate safety measures must be taken.

The complexes showed only ill-defined decomposition points on heating.

$[Mn(XBP)(NO_3)_2] \cdot 2H_2O$

A solution of $Mn(NO_3)_2 \cdot 4H_2O$ (0.1 mmol, 0.025 g) and XBP (0.1 mmol, 0.036 g) in methanol (6 mL) was allowed to evaporate slowly over concentrated H_2SO_4 in a desiccator. Yellow “sea-urchin-like” clusters of microcrystals were formed within 2 weeks; these were collected and dried under reduced pressure.

$[Mn(XBP)Cl_2] \cdot 2.5H_2O$

Solutions of $MnCl_2 \cdot 4H_2O$ (0.1 mmol, 0.020 g) and XBP (0.1 mmol, 0.036 g) each dissolved in a 1 : 1 mixture of methanol (2 mL) and 2,2-

dimethoxypropane (2 mL) were mixed and stirred for 30 min, resulting in the formation of a white suspension. Addition of methanol (3 mL) gave a clear solution. This was allowed to concentrate as above and yellow microcrystalline globules formed over a period of several days.

$[Mn(XBP)Br_2]\cdot H_2O$ *and* $[Co(XBP)Br_2]$

Warm solutions of $MnBr_2 \cdot 4H_2O$ (0.1 mmol, 0.029 g) or $CoBr_2 \cdot 6H_2O$ (0.1 mmol, 0.033 g), respectively, each in ethanol (3 mL), were added slowly, with stirring, to a similar ethanolic solution of XBP (0.2 mmol, 0.072 g, in 3 mL) followed by stirring at 50 °C for 1 hr. The cream-coloured (Mn) or dark blue (Co) powders which formed were filtered off, washed with ethanol, and dried over silica gel under reduced pressure.

$Mn(XBP)_2(ClO_4)_2 \cdot 3H_2O$

A solution of manganese(II) perchlorate hexahydrate (0.033 mmol, 0.012 g) and XBP (0.1 mmol, 0.036 g) in methanol (6 mL) was allowed to concentrate overnight over concentrated H_2SO_4 in a desiccator. The yellow "feathery" crystals which formed were collected and air-dried.

$[Co(XBP)(NO_3)_2]$

A solution of $Co(NO_3)_2 \cdot 6H_2O$ (0.1 mmol, 0.029 g) and XBP (0.1 mmol, 0.036 g) in a mixture of methanol (2 mL) and acetonitrile (4 mL) was allowed to evaporate slowly over concentrated H_2SO_4 in a desiccator. The purple, microcrystalline globules which separated over 1 week were collected and dried under reduced pressure.

$[Co(XBP)Cl_2]\cdot H_2O$

A solution of $CoCl_2 \cdot 6H_2O$ (0.1 mmol, 0.024 g) in acetonitrile (3 mL) was mixed with one of XBP (0.1 mmol, 0.036 g) in a mixture of methanol (1 mL) and acetonitrile (3 mL). The resulting blue suspension was stirred for *ca.* 1 hr and then centrifuged to remove the blue solid which was dried under reduced pressure.

$[M(XBP)I_2]$ $(M = Co, Zn)$

A 0.1 M solution of the respective metal iodide in ethanol was prepared *in situ* from sodium iodide and the hydrated Co or Zn nitrate. An aliquot (1 mL) containing 0.1 mmol of the respective metal iodide (0.031 g for Co, 0.032 g for Zn) was added dropwise to a warm solution of XBP (0.2 mmol, 0.072 g) in ethanol (4 mL). The dark blue (Co) or yellow (Zn) powders which separated within several hours were filtered off, washed with ethanol, and dried over silica gel under reduced pressure.

[Co(XBP)(NCS)$_2$] · 0.5H$_2$O

The mixing of solutions of cobalt(II) thiocyanate (0.1 mmol, 0.018 g) and XBP (0.2 mmol, 0.072 g) in warm ethanol (4.2 mL) resulted in the formation of a dark blue precipitate which was collected as for [M(XBP)I$_2$] (M = Co, Zn).

Ni(XBP)Cl$_2$ · H$_2$O

A hot solution of $NiCl_2 \cdot 6H_2O$ (0.1 mmol, 0.024 g) in butan-1-ol (3 mL) was added dropwise to a similar solution of XBP (0.2 mmol, 0.072 g, in 3 mL). A blue-green precipitate formed instantly. Stirring was maintained under gentle reflux for *ca.* 3 hr and the mixture was then centrifuged to separate the solid. The complex was washed with diethyl ether and dried under reduced pressure.

M(XBP)$_2$(ClO$_4$)$_2$ · 2H$_2$O (M = Ni, Zn)

A solution of the respective metal perchlorate hexahydrate (0.033 mmol, 0.012 g) in acetonitrile (4 mL) was added dropwise to a solution of XBP (0.1 mmol, 0.036 g) in a mixture of methanol (1 mL) and acetonitrile (3 mL). The nickel complex separated as a fine, green powder over a period of 3–4 days. The solution of the zinc complex was filtered after 3 days and the resulting solution deposited colourless crystals during the following 36 hr.

Cu(XBP)Cl$_2$ · 2.5H$_2$O

Methanolic solutions of $CuCl_2 \cdot 2H_2O$ (0.1 mmol, 0.017 g, in 3 mL) and XBP (0.1 mmol, 0.036 g, in 3 mL) were mixed and stirred for *ca.* 1 hr. The resultant greeny-yellow powder was collected by centrifuging and dried under reduced pressure.

Cu(XBP)Br$_2$ · 1.5H$_2$O

This was obtained by essentially the same method as for the bromide complexes of Mn(II) and Co(II) but with cold methanol as the solvent.

[Cu$_2$(XBP)$_3$(NO$_3$)$_2$](NO$_3$)$_2$ · 2H$_2$O

A solution of $Cu(NO_3)_2 \cdot 3H_2O$ (0.1 mmol, 0.024 g) in a mixture of methanol (1 mL) and acetonitrile (3 mL) was added slowly to a similar solution of XBP (0.1 mmol, 0.036 g, in 4 mL of solvent mixture). A green cloudiness may be produced by too rapid addition of the metal salt solution and this can be cleared by dropwise addition of methanol. The clear solution was allowed to concentrate slowly over concentrated H_2SO_4 in a desiccator and green crystals formed over 4–5 days.

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$Zn_2(XBP)_3(NO_3)_4 \cdot 4H_2O$

A hot solution of $Zn(NO_3) \cdot 6H_2O$ (0.1 mmol, 0.030 g) in ethanol (3 mL) was added dropwise with stirring to one of XBP (0.2 mmol, 0.072 g) also in ethanol (3 mL). A cream-coloured solid formed instantly. Stirring was maintained under gentle reflux for a further 3 hr after which the solid was collected by centrifuging. It was washed with diethyl ether and dried under reduced pressure.

$Zn(XBP)Cl_2 \cdot H_2O$

An aqueous solution of zinc(II) chloride (0.1 mmol, 0.014 g, in 3 mL) was added dropwise to a solution of XBP (0.1 mmol, 0.036 g) in a mixture of water (5 mL) and methanol (2 mL). The clear solution was left to evaporate slowly over concentrated H_2SO_4. Florets of small crystals formed over a period of several days and these were air-dried.

$Cd(XBP)_3(ClO_4)_2 \cdot 2MeCN \cdot 2H_2O$

Dropwise addition of a solution of $Cd(ClO_4)_2 \cdot 6H_2O$ (0.033 mmol, 0.014 g) in acetonitrile (4 mL) to a solution of XBP (0.1 mmol, 0.036 g) in a mixture of methanol (1 mL) and acetonitrile (3 mL) gave an immediate cream-coloured precipitate. Methanol (*ca.* 1 mL) was added dropwise until the precipitate redissolved. The resulting clear solution was allowed to concentrate in a desiccator over concentrated H_2SO_4; pale yellow crystals formed overnight.

$M_4(XBP)_7(NO_3)_{12} \cdot 4H_2O$ (M = La, Ce, Pr, Nd, Sm, Eu) and
$M_2(XBP)_3(NO_3)_6 \cdot 2H_2O$ (M = Gd, Tb, Dy, Ho, Er, Yb)

A methanolic solution of the hydrated lanthanide(III) nitrate (0.1 mmol in 3 mL) was added slowly to one of XBP (0.2 mmol, 0.072 g) also in methanol (3 mL) and the resulting milky suspension stirred for 2 hr. The fine powders which formed were filtered off, washed with cold methanol, and dried under reduced pressure.

$M_2(XBP)_3Cl_6 \cdot 8H_2O$ (M = Pr, Nd)

A solution of $PrCl_3 \cdot 7H_2O$ (0.067 mmol, 0.025 g) or $NdCl_3 \cdot 6H_2O$ (0.067 mmol, 0.024 g), respectively, each in a mixture of methanol (1 mL) and acetonitrile (2 mL), was added to a similar solution of XBP (0.2 mmol, 0.072 g) resulting in the immediate formation of a cloudy suspension. Methanol was added dropwise until complete dissolution was achieved (*ca.* 2 mL required). The resulting clear solution was allowed to evaporate slowly over concentrated H_2SO_4 in a desiccator. After 1–2 days a small quantity of fine powder had reformed and this was filtered off and the filtrates were left to concentrate as before. Clusters of "canoe-shaped" crystals formed over a further

3–4 day period. These were collected, washed with cooled acetonitrile, and air-dried.

$Eu_2(XBP)_3Cl_6 \cdot 2H_2O$

The synthetic route was essentially the same as for the previous two compounds but microcrystalline globules of the cream-coloured Eu complex formed overnight from the initial reaction mixture. These were collected, washed with acetonitrile, and dried under suction.

$M_2(XBP)_3Cl_6 \cdot nH_2O$ ($M = Tb$, $n = 2$; $M = Dy$, Yb, $n = 0$)

These were also obtained by the same method as for the europium chloride complex but in these cases the reaction mixture which turned cloudy immediately was stirred for approximately two and a half hours and then centrifuged to separate the solid complex. The resulting fine powders were washed with diethyl ether and dried over silica gel under reduced pressure.

$M(XBP)_3(ClO_4)_3 \cdot 2H_2O$ ($M = Y$, Dy); $M_2(XBP)_7(ClO_4)_6 \cdot nH_2O$ ($M = La$, Gd, $n = 7$; $M = Sm$, $n = 4$)

A methanolic solution of the hydrated lanthanide(III) perchlorate (0.04 mmol in 3 mL) was added slowly to one of XBP (0.2 mmol, 0.072 g) also in methanol (3 mL) and the resulting milky suspension stirred for 2 hr. The fine powders which formed were filtered off, washed with cold methanol, and dried under reduced pressure.

$Nd_2(XBP)_7(ClO_4)_6 \cdot 7H_2O$

A solution of $Nd(ClO_4)_3 \cdot 6H_2O$ (0.04 mmol, 0.022 g) in a mixture of methanol (1 mL) and acetonitrile (2 mL) was added to a similar solution of XBP (0.2 mmol, 0.072 g, in 3 mL). The white precipitate which formed instantly was redissolved by addition of methanol (4 mL) and water (1 mL). The resulting clear solution was allowed to evaporate at room temperature, filtered after *ca.* 1 week to remove a small amount of mauve powder and then left to concentrate further. After a further week the florets of pale mauve crystals which had formed were collected and air-dried.

Analyses and Physical Measurements

Microanalyses were by the Microanalytical Service, Department of Chemistry, Imperial College. EPR spectra were measured on powdered solid state samples at room temperature using a Varian E12 X-band (*ca.* 9.5 GHz) spectrometer. Infrared spectra were measured on a Research Series Fourier Transform spectrometer as Nujol mulls between CsI plates. Solid state electronic spectra were measured by the reflectance method over the range 4000–30,000 cm^{-1} using a Beckman DK2 spectrometer and the standard reflectance accessory. Luminescence spectra were recorded on powdered solid state samples using a Perkin–Elmer LS50 luminescence spectrometer fitted with the standard solid state sample accessory. The phosphorescence lifetimes were obtained by recording the decay of the emission band intensities (as designated in Table 4) over twenty 0.1 msec intervals for the terbium complexes and at 0.01 msec intervals for the other complexes. In each case, a plot of the natural logarithm of the phosphorescence intensity against time gave a straight line, the gradient of which is equal to the reciprocal of the phosphorescence lifetime. The x-ray powder diffraction pattern of $Cd(XBP)_3(ClO_4)_2 \cdot 2MeCN \cdot 2H_2O$ was obtained with a Siemens D-500 powder diffractometer.

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