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Metal Complexes of Azopyridines, Part V. Spectroscopic Studies on Cobalt(II) Complexes of 2,2′-Azopyridine

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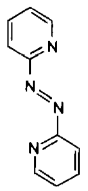
It is known that 2,2′-azopyridine (I) is a very versatile ligand which forms complexes with metal salts having metal:ligand ratios 1:3, 1:2, 1:1, and even 2:1 [1–3]. The co-ordination centres can be a pyridine group or groups, an azo-nitrogen atom or atoms, or various combinations of these. Because of insolubility of the complexes and inability to obtain samples suitable for single-crystal X-ray diffraction, spectroscopic studies in the solid state are the only practical means available for probing which mode of co-ordination of the ligand is adopted in the various cases. The co-ordination geometry of the metal atoms may often be deduced comparatively easily by study of electronic spectra, but this of itself usually still results in ambiguity concerning the azopyridine co-ordination sites. However, the careful study of far-infrared spectra, and of the multiplicity and shifts of mid-infrared bands associated with internal modes of vibration of the pyridine rings, can lead to fairly clear structural conclusions [3].



(I)

Cobalt salts afford compounds covering the known full range of metal:ligand ratios (Table I), and a study of such complexes has therefore been undertaken to seek further information concerning 2,2′-azopyridine (L) co-ordination.

Experimental

The ligand 2,2′-azopyridine was prepared as described previously [2]. It crystallised from light petroleum (b.p. 60–80°) as deep red needles, m.p. 87°.

Complexes CoX_2L were prepared by mixing methanolic and ethanolic solutions of the metal salts and the organic ligand in the required proportions. For complexes CoX_2L_2, the ligand was kept in slight excess of the stoicheiometric requirement, whereas for $(CoX_2)_2L$ the cobalt(II) salt was in small excess.

None of the complexes was significantly soluble in solvents which did not cause extensive decomposition, and therefore they could not be recrystallised nor could reliable physical measurements be carried out on solutions.

Physical measurements were obtained as previously described [4].

TABLE I. Analytical Data.

Compound	Colour	μ_{eff}/BM[a]	Analytical Data (%)					
			Found			Calculated		
			Co	N	C	Co	N	C
$Co(ClO_4)_2L_3$	brown	4.8	7.3	20.0	43.8	7.3	20.7	44.4
$Co(ClO_4)_2L_2$	dark-green	5.0	9.4	18.1	37.8	9.4	18.5	38.3
$CoCl_2L_2$	crimson	4.4	11.9	22.1	47.9	11.8	22.4	48.2
$CoBr_2L_2$	red-brown	4.5	10.3	19.2	41.4	10.3	19.0	40.9
$Co(NCS)_2L_2$	red-brown	5.1	10.8	25.0	47.9	10.8	25.8	48.6
$Co(NO_3)_2L_2$	dark-brown	5.0	10.6	25.0	42.8	10.7	25.4	43.5
$CoCl_2L$	dark-green	4.3	18.7	17.9	38.5	18.7	17.8	38.1
$CoBr_2L$	dark-brown	4.5	14.5	13.8	29.8	14.6	13.9	29.8
$Co(NO_3)_2L$	dark-brown	4.9	15.8	22.6	31.9	16.0	22.9	32.6
$(CoCl_2)_2L$	green	4.4	26.2	12.8	27.5	26.6	12.6	27.1
$(CoBr_2)_2L$	dark-green	4.4	19.3	9.2	19.7	19.0	9.0	19.3

[a] At room temperature.

TABLE II. Electronic and Far-Infrared Spectral Data.

Compound	$\nu_{electronic}/10^3$ cm^{-1}	ν(CoX)^a/cm^{-1}	ν(CoN)/cm^{-1}
L	46.3, 36.5, 31.0, 29.4, 27.8, 21.3		
$Co(ClO_4)_2L_3$	45.0, 35.0, 31.2, 26.0, 16.4, 9.5		259, 244, 233
$Co(ClO_4)_2L_2$	44.6, 37.0, 32.0, 25.6, 16.8, 10.2	210^d	230^d
$CoCl_2L_2$	45.0, 30.3, 20.33, *ca.* 14.3^b, 9.76^c	236^d	260^d
$CoBr_2L_2$	45.0, 38.5^b, 32.0, 25.5^b, 20.0, *ca.* 17.59^b, 10.1, 8.06^b	206, 192	257, 230
$Co(NCS)_2L_2$	45.0, 35.8, 31.2, 25.0, 17.5, 9.8	239^d	259^d
$Co(NO_3)_2L_2$	45.0, 37.8, 31.8, 27.0, 22.2, 16.2, 10.5		236
$CoCl_2L$	45.0, 35.0^b, 29.4, 24.5^b, 17.7, *ca.* 14.9^b, 8.07	276, 264	225
$CoBr_2L$	44.0^b, 38.5^b, 28.5, 24.93^b, 17.76^b, 14.3^b, 8.2	244, 223^d	209^d
$Co(NO_3)_2L$	45.0, 37.3, 32.2, 26.3, 17.8, 9.4	276	
$CoCl_2)_2L$	44.0, 26.0, 16.2, 11.63, 5.78, 4.48	332, 324, 282	200
$(CoBr_2)_2L$	44.0^b, 38.0^b, 24.4, 16.29, *ca.* 11.36^b, *ca.* 9.52^b, 5.62, 4.46	266, 249, 223	200

[a] X = anion. [b] Shoulder. [c] Asymmetric. [d] These assignments might possibly be reversed.

TABLE III. Mid-Infrared bands (cm^{-1}) Arising from Internal Ligand Vibrations of the Pyridine Rings[a].

Compound	8a	19b	18b	1	10b	4	6b	16a
L	1582 s	1428 s	1095 s	991 s	799 s	740 s	627 s	407 s
$Co(ClO_4)_2L_3$	1605 s 1589 s	1440 s 1420 m		1012 m 993 m	799 s 780 sh	742 s 725 sh	642 s	425 m 411 w
$Co(ClO_4)_2L_2$	1603 s 1582 s	1441 s 1419 m		1012 m 995 m	795 s 785 sh	742 s 725 m	640 m	425 s 412 m
$CoCl_2L_2$	1599 s 1579 s	1438 s 1409 m	1099 m 1085 m	1010 s 985 m	799 s 780 s	738 s 722 m	642 s 628 m	430 m 411 m
$CoBr_2L_2$	1602 s 1590 s	1445 s 1420 m	1099 m 1089 m	1015 s 992 m	787 s 786 m	744 s 739 s	639 s 625 m	430 m 411 m
$Co(NCS)_2L_2$	1605 s 1585 s	1442 s 1417 m	1095 s	1020 s 996 s	791 s 776 w	739 s 728 s	641 m	425 s 406 m
$Co(NO_3)_2L_2$	1600 s 1580 s		1100 m 1090 sh	1014 s 990 m	791 s 785 sh		645 m	424 m 410 m
$CoCl_2L$	1600 s	1440 s	1098 s	1018 s	790 s	740 s	642 m	430 m
$CoBr_2L$	1601 s	1438 s	1098 m	1015 s	790 s	739 s	642 s	424 m
$Co(NO_3)_2L$	1600 m	1435 s	1103 m	1018 s	790 s	739 m	650 m	426 m
$(CoCl_2)_2L$	1600 m	1445 m	1097 s	1026 s	798 s	739 m	625 m	419 m
$(CoBr_2)_2L$	1600 s	1441 m	1099 m	1026 s	796 s	742 m	650 m	416 m

[a] The designations '8a' *etc.* follow those previously adopted [3]; s = strong, m = medium, w = weak, sh = shoulder.

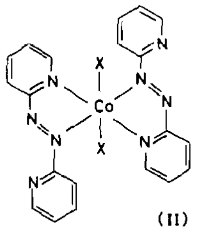
Results and Discussion

The only 1:3 complex obtained, $Co(ClO_4)_2L_3$, shows, in the electronic spectrum (Table II), weak *d–d* bands below *ca.* 10 000 cm^{-1}, well-resolved from the strong absorption edge of the ultra-violet region, of relatively low intensity typical of pseudooctahedral complexes. Splitting of the mid-infrared spectral bands due to the pyridine groups (Table III) demonstrates [3] that both 'free' and co-ordinated pyridine nitrogen atoms are present, but apart from the implication that azo-nitrogen atoms must therefore be acting as donor centres, no further structural conclusions are warranted.

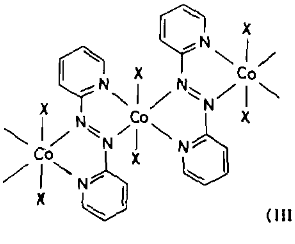
For CoX_2L_2 (X = Cl, Br, ClO_4, NO_3, or NCS), the electronic spectra (Table II) are again typical of cobalt(II) in a hexaco-ordinate environment. The expected distortion from O_h symmetry is most marked for the bromide, where splitting of the $^4T_{2g}$ level gives rise to clear resolution (rather than broadening as in the chloride) of the lowest energy band (8060 and 10100 cm^{-1}). A similar lowering of symmetry was noted for polymeric hexaco-ordinate 1:1 complexes of 3,3'- and 4,4'-azopyridines [4] and for complexes of type CoX_2L_4 (L = unidentate heterocyclic amine) [5]. The mid-infrared spectra (Table III) show the same effect as for $Co(ClO_4)_2L_3$, *i.e.* splitting of pyridine ring modes with band positions characteristic of an azopyridine ligand having only one of the ring nitrogen atoms co-ordinated [3]. Thus the structures of the CoX_2L_2 complexes must involve *either* terminal anionic groups and bidentate azopyridines (chelating or bridging), *or* bridging anionic groups and unidentate azopyridines. Consideration of the positions of the ν(CoX) modes in the far-infrared spectra (Table II) rules out the latter possibility for the halides at least. Thus ν(CoX) at 236 (or 260) cm^{-1} for the chloride, and 192, 206 cm^{-1} for the bromide, are more typical of terminal halide groups in hexaco-ordinated systems such as in $CoX_2(pyridine)_4$ [6], $CoX_2(hydrazine)_2$ [6] and $CoX_2(pyrazine)_2$ [7, 8] than of halogen-bridged systems as found for $CoX_2(pyridine)_2$ [9], CoX_2(pyrazine) [9] and CoX_2(4,4'-dipyridylethylene) [10]. Structure (II), involving L chelating, is therefore strongly indicated, since bridging of the amine ligand via one azo-group and one ring nitrogen atom, to give a structure analogous to $CoX_2(pyrazine)_2$ [7], is structurally not possible. It is noteworthy that the distortion observed for $CoBr_2L_2$ from the electronic spectrum is supported by the presence of two well resolved bands for both ν(CoBr) and ν(CoN), only one of each type being expected for a regular (D_{4h}) CoX_2N_4 skeleton.

For CoX_2L (X = Cl, Br, I, or NO_3), octahedral co-ordination of the metal is again indicated by the electronic spectra, but in these cases the mid-infrared spectra clearly show that only one type of pyridine group is present and is in a co-ordination position. The stoicheiometry thus requires *either* terminal anionic groups with azopyridines both chelating *and* bridging (*i.e.* each using all four nitrogen atoms in co-ordination) as in structure (III), *or* bridging anionic groups and bridging azopyridines (each co-ordinated by the two-ring nitrogen atoms). The far-infrared spectra of these compounds are curious, since although the ν(CoX) modes identified [264, 276 cm^{-1} (X = Cl); 223, 244 cm^{-1} (X = Br)] are plainly at much higher wavenumbers than in known halide-bridged systems (*e.g.* for chlorides: $CoCl_2(pyridine)_2$, 177 and 192 cm^{-1} [9]; $CoCl_2$(pyrazine), 179 and 209 cm^{-1} [9]; $CoCl_2$(3,3'-azopyridine), *ca.* 185–215 cm^{-1} [4]), pointing to structure (III), they are also at significantly higher wavenumbers than in octahedral cobalt(II) compounds containing terminal halide groups [6–8]. In particular, it is noteworthy that the ν(CoX) spectra are quite different to those of the analogous CoX_2L_2 compounds (Table II), even though the environment of cobalt required for structure (III) is analogous to that in (II). The only way in which all the experimental data can be accommodated is for the compounds CoX_2L to be of type (III), with bonding to the azo-groups being significantly weaker than in (II), as would be expected from the presence of a small steric hinderance resulting from the participation of all nitrogen atoms, leading to a strengthening of the Co–X bonds and a corresponding raising of ν(CoX). Evidently the Co–N(azo) interaction is still sufficiently important to give electronic spectra characteristic of octahedral co-ordination. A weak band at 326 cm^{-1} in the spectrum of $CoCl_2L$, which has no counterpart in the other spectra, is indicative of a ν(CoCl) mode of tetrahedral end-groups of the $[CoCl_2L]_n$ chains.

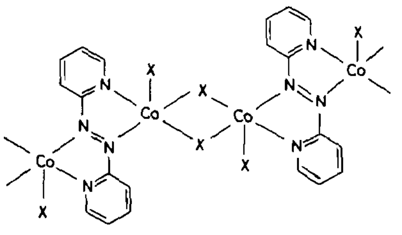
An even more unusual situation is found for $(CoX_2)_2L$ (X = Cl or Br). The electronic spectra show a pair of strong bands in the 4000–6000 cm^{-1} region, medium intense absorption at 9500–12000 cm^{-1}, and a pair of apparently strong bands at 16200 cm^{-1} (on the edge of the strong ultraviolet absorption). These features are unlike those of tetrahedral or octahedral co-ordination of cobalt(II), but are similar to those found for pentaco-ordinate, square pyramidal cobalt(II) complexes, pointing to the same geometry in these cases [11]. From mid-infrared spectral measurements we conclude that both of the pyridine rings of each azopyridine are co-ordinated. The far-infrared spectra show unambiguously that *terminal* cobalt–halogen bonds are present, with ν(CoCl) at 324, 332 cm^{-1} and ν(CoBr) at 249, 266 cm^{-1}. However, the other data require *bridging* halogen atoms to be present for this stoicheiometry. Bands at 282 cm^{-1} (X = Cl) and 223 cm^{-1} (X = Br) are likely to be of this origin, $\nu(CoX)_b$, and the fact that they are at significantly higher wavenumbers than in known (octahedral) bridged systems is fully explicable in terms of the lower co-ordination number (square pyramidal) in the present cases. The only structure



(II)



(III)



(IV)

which we find is compatible with the experimental data is of the type shown as (IV), which is analogous to that proposed for the $(CuX_2)_2L$ analogues [3].

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