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Complexes of Acridine N-oxide with Some Transition Metal and Group IIb Metal Halides, Thiocyanates and Nitrates

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Acridine N-oxide forms complexes having 1:1 or 1:2 metal: ligand stoichiometry with Mn(II), Co(II), Ni(II), Zn(II) or Hg(II) halides, thiocyanates or nitrates. Unlike corresponding pyridine N-oxide or quinoline N-oxide systems, no products were obtained having more than two acridine N-oxide molecules per metal ion, or containing additional co-ordinated water or solvent molecules. The preference of acridine N-oxide for 1:1 or 1:2 complexes appears to be the result of insolubility, rather than steric or electronic, effects. In tetrahedral complexes (e.g. [$CoCl_2(aco)_2$]), metal–oxygen and metal–chlorine stretching vibrations are assigned between 300–400 cm^{-1}. Octahedral complexes (e.g. [$CoCl_2(aco)$]) have ligand-bridged structures and their i.r. spectra contain no identifiable metal–ligand bands above 300 cm^{-1}. It is suggested that a vibration at 1085 cm^{-1} in the i.r. spectrum of acridine N-oxide contains a substantial contribution from the N–O stretching co-ordinate.

Introduction

Acridine N-oxide (aco) is potentially an interesting ligand because of its rather severe steric requirements. Popp, Nathan, McKean and Ragsdale[1] have prepared a number of first-row transition metal perchlorate complexes and observe that these tend to contain only four co-ordinated acridine N-oxide molecules, whereas the same acceptors will readily combine with six molecules of pyridine N-oxide (pyo)[2] or quinoline N-oxide (qno)[3]. There is also some evidence that acridine N-oxide tends to form five-coordinate rather than six-coordinate complexes with certain diorganotin compounds[4]. We have now studied the reactions of acridine N-oxide with a number of transition metal and Group IIb metal halides, thiocyanates and nitrates, all of which form well-characterised pyridine N-oxide and quinoline N-oxide complexes.[2,5–8]

Experimental

Acridine N-oxide was prepared by oxidation of acridine with perbenzoic acid, using the method of Acheson *et al.*[9]

Acridine N-Oxide Complexes

These were obtained from ethanol solutions containing the appropriate hydrated metal salt and acridine N-oxide in 1:2 molar proportions. The solutions were boiled for 2–3 minutes and allowed to stand for at least 1 hour, during which the solid complexes separated. Use of excess acridine N-oxide yielded the same products, usually contaminated with free ligand. The 1:1 complex [$CoCl_2$ (aco)] was obtained from a solution containing a fivefold excess of cobalt(II) chloride. Analytical and physical data for the complexes are given in Table I.

Spectroscopic Data

The visible and i.r. spectra were obtained using nujol mulls with Unicam SP700 or Perkin–Elmer 457 spectrophotometers.

Results and Discussion

Details of the vibrational spectra of the complexes are given in Table II. The assignment of the N–O stretching vibration in acridine N-oxide is not entirely straightforward because the N–O and ring vibrations are likely to mix to some extent. In quinoline N-oxide this effect is so pronounced that no vibration can be labelled, even approximately, as an 'N–O stretch'.[10] A strong band at 1328 cm^{-1} in the i.r. spectrum of acridine N-oxide is usually taken to be due to the N–O stretching vibration:[1,11] on complex formation this band often splits and shifts slightly. A second strong band (assigned[11] to a CNO mode with considerable C–N stretching character) also shifts, by 5–30 cm^{-1} to lower frequency, on co-ordination. Over the whole series of complexes, the behaviour of the 1085 cm^{-1} band is less erratic than that of the 1328 cm^{-1} band,

TABLE I. Acridine N-Oxide Complexes.

	Found %				Calc %				M.P. °C	Colour
	C	H	M	X[a]	C	H	M	X		
$[MnCl_2(aco)]$	48.7	3.1	17.0	22.0	48.6	2.8	17.1	22.1	270	Green
$[Mn(NO_3)_2(aco)_2]$	55.1	3.5	9.3		54.9	3.2	9.6		188	Green
$[Mn(NCS)_2(aco)_2]$	61.0	3.2		20.3	59.9	3.2		20.7	256	Green
$[CoCl_2(aco)]$	48.9	2.9	17.9	22.2	48.0	2.8	18.1	21.8	290	Brown
$[CoCl_2(aco)_2]$	60.1	3.5	11.4	13.5	60.0	3.5	11.3	13.6	265	Green
$[CoBr_2(aco)_2]$	51.3	3.3	9.7	26.8	51.3	3.0	9.9	26.3	256	Green
$[Co(NCS)_2(aco)_2]$	60.0	3.2	10.1	20.1	59.7	3.2	10.4	20.5	241	Red
$[Co(NO_3)_2(aco)_2]$	54.6	3.1	10.4		54.5	3.2	10.3		232	Red
$[NiCl_2(aco)]$	47.2	3.0		21.2	48.0	2.8		21.8	320	Red
$[NiBr_2(aco)]$	37.3	2.5		38.7	37.7	2.2		38.7	295	Dark Red
$[Ni(NCS)_2(aco)]$	49.1	2.7	15.6	31.0	48.7	2.5	15.8	31.4	265	Green
$[ZnCl_2(aco)_2]$	59.3	3.4		13.2	59.3	3.4		13.5	220	Yellow
$[Zn(NO_3)_2(aco)_2]$	53.5	3.3			53.9	3.1			205	Yellow
$[HgCl_2(aco)]$	33.5	1.8		15.5	33.4	1.9		15.2	256	Yellow
$[HgBr_2(aco)]$	28.5	1.8		29.8	28.1	1.6		29.4	238	Yellow
$[Hg(NCS)_2(aco)]$	34.8	1.8			35.2	1.8			159	Yellow

[a] X = Cl, Br, NCS.

and it is also more obviously comparable with the behaviour of the N–O stretching mode in analogous pyridine N-oxide complexes.[2,6] The two acridine N-oxide bands shift in opposite directions in 9-substituted derivatives,[11] (*e.g.* in 9-methoxyacridine N-oxide the 1328 cm^{-1} band increases to 1365 cm^{-1} whereas the 1085 cm^{-1} band drops to 1076 cm^{-1}). The shifts in the 1085 cm^{-1} band are in the same sense as those observed in the N–O stretch in 4-substituted pyridine N-oxides,[12] and are generally similar in magnitude. Accordingly although the 1328 cm^{-1} and 1085 cm^{-1} vibrations will undoubtedly both have N–O stretching character, we suggest that the N–O stretching co-ordinate makes its major contribution to the 1085 cm^{-1} mode.

The low-frequency i.r. spectrum of acridine N-oxide contains a strong band at 361 cm^{-1}. The spectra of the complexes consistently exhibit either a broad strong band, or two resolved bands, between 370–345 cm^{-1}. In a few cases there may be overlaps with metal–ligand bands but except where there is firm evidence to the contrary we have assigned the bands in this region to internal ligand vibrations. There are no other obvious internal ligand absorptions below 395 cm^{-1}.

The electronic spectra of the complexes (Table III) are dominated by intense ligand and c.t. absorptions which extend from maxima around 21000 cm^{-1} into the visible region, obscuring many of the weaker *d–d* bands. As a result, only a limited amount of useful structural information can be obtained from the visible spectra.

The 1:2 complexes $[CoX_2(aco)_2]$ (X = Cl, Br, NCS) are typical tetrahedral cobalt(II) complexes with relatively strong, well defined visible absorption bands near 16000 cm^{-1}. The Co–Cl and Co–Br stretching vibrations occur within the usual frequency range for tetahedral Co(II) halide complexes.[13] The frequency of the C–N stretching vibration in the thiocyanato complex is indicative of terminal, N-bonded thiocyanate.[14] Each of the complexes has a strong sharp band near 380 cm^{-1} which we assign to a Co–O stretching mode: this is about 50 cm^{-1} lower than the Co–O stretching frequencies reported for tetrahedral $[CoX_2(Ph_3AsO)_2]$ (X = Cl, Br).[15] For a C_{2v} (CoO_2X_2) environment we would expect to observe two i.r.-active Co–O stretching vibrations. The Co–O stretching bands in $[CoBr_2(qno)_2]$ and $[CoI_2(qno)_2]$ appear as doublets between 370–390 cm^{-1}, but $[CoCl_2(qno)_2]$ has only a single fairly sharp band at 387 cm^{-1}. The second Co–O band in the acridine N-oxide complexes may be hidden by the ligand absorption near 360 cm^{-1} but there is also a strong band near 300 cm^{-1} in the spectra of all three complexes. In the chloro- or thiocyanato complexes this band could readily be assigned as a Co–Cl or Co–N stretching vibration but it appears equally strongly at 300 cm^{-1} in the spectrum of the bromo complex, where the Co–Br stretch cannot reasonably be placed above 250 cm^{-1}. Therefore, in spite of its unusually low frequency we suggest that the 300 cm^{-1} band may be associated with a Co–O stretching vibration. The zinc complex $[ZnCl_2(aco)_2]$ has an i.r. spectrum very similar to that of $[CoCl_2(aco)_2]$ and the Zn–Cl stretching frequencies are in the expected range for tetrahedrally coordinated zinc.[13]

The 1:1 complexes $[MnCl_2(aco)]$, $[CoCl_2(aco)]$ and $[NiX_2(aco)]$ (X = Cl, Br, NCS) have weak *d–d*

TABLE II. I.r. Spectra: N–O Stretching, Metal–Ligand Stretching and Internal Anion Vibrations (cm^{-1}, nujol mulls).

	νN–O		νMetal–Ligand^a				Ligand Vibrations	Anion Vibrations	
Acridine N-oxide	1328 s	1085 s					360 s		
Tetrahedral Complexes									
[CoCl$_2$(aco)$_2$]	1328 s	1067 s	380 ms	Co–O	328 s	Co–Cl	366 s^b		
	1320 sh		306 s	Co–O?	298 s	Co–Cl	345 sh, w		
[CoBr$_2$(aco)$_2$]	1327 s	1075 sh	380 s	Co–O	250 s	Co–Br	365 s^b		
	1319 sh	1065 s	300 s	Co–O			345 sh		
[Co(NCS)$_2$(aco)$_2$]	1332 s	1072 s	381 s	Co–O	280 s, br	Co–N	358 s^b	νCN	2060
	1326 s	1068 s	300 s	Co–O?	270 sh				
[ZnCl$_2$(aco)$_2$]	1325 s	1078 s	378 m	Zn–O	321 s	Zn–Cl	366 m^b		
	1319 sh		305 m	Zn–O?	280 m	Zn–Cl	350 mw		
Ligand-bridged Complexes									
[CoCl$_2$(aco)]	1325 s	1068 s	270 m	Co–O			365 m		
			265 m, br	Co–O			350 w		
[NiCl$_2$(aco)]	1322 s	1073 s	285 sh	Ni–O			370 s^b		
			268 s, br	Ni–O			349 mw		
[NiBr$_2$(aco)]	1320 s	1068 s	280 sh	Ni–O			370 s^b		
			265 m, br	Ni–O			348 mw		
[Ni(NCS)$_2$(aco)]	1326 sh	1079 s	295 m	Ni–X			360 s^b	νCN	2140 s
	1319 s		289 m, br	Ni–X			349 mw		2120 s
[MnCl$_2$(aco)]	1326 s	1071 s	260 s	Mn–O			351 m		
	1319 sh						343 sh		
[Mn(NCS)$_2$(aco)$_2$]	1327 s	1085 s	290 m, br	Mn–X			360 s	νCN	2060 s
		1069 s	270 m, br	Mn–X					
			250 m, br	Mn–X					
Other Complexes									
[Co(NO$_3$)$_2$(aco)$_2$]	1330 s	1080 s	338 m	Co–X			369 m	NO$_3$	1485 s
	1320 sh	1072 sh	298 s	Co–X					1297 s, 1275 s
			260 m, br	Co–X					1022 m
									811 m
[Mn(NO$_3$)$_2$(aco)$_2$]	1325 s	1080 m	320 w	Mn–X			360 s, br	NO$_3$	1475 s
	1318 s	1060 s	280 sh	Mn–X					1305 s
			270 s	Mn–X					1030 m
			252 m	Mn–X					815 m
[Zn(NO$_3$)$_2$(aco)$_2$]	1330 s	1080 s	345 mw	Zn–X			360 m	NO$_3$	1490 s
			298 m	Zn–X					1300 s, 1280 s
			260 m, br	Zn–X					1020 s
									812 m
[HgCl$_2$(aco)]	1320 sh	1080 s	340 vs, br	Hg–Cl					
	1315 s		250 m	Hg–X					
[HgBr$_2$(aco)]	1320 sh	1068 s	258 m	Hg–Br			354 ms		
	1315 s						340 m		
[Hg(CNS)$_2$(aco)]	1322 s	1078 s	320 w	Hg–X			358 m	νCN	2130 s
			299 m, br	Hg–X					
			250 m	Hg–X					

[a] M–X indicates that it is not practicable to dinstinguish between M–aco and M–anion modes. [b] Possible coincidence with M–O vibration.
s = strong, m = medium, w = weak, br = broad, sh = shoulder.

spectra, the individual bands being distinguishable above the c.t. background only in the case of [Ni(NCS)$_2$(aco)]. The low-frequency i.r. spectra are very different from those of the tetrahedral complexes and contain no abviously identifiable metal–ligand bands above 290 cm^{-1}. Between 250–290 cm^{-1} there are a series of rather broad absorption bands which occur at almost identical frequencies in [NiCl$_2$(aco)]

TABLE III. Visible Absorption Spectra (nujol mulls). Maxima of Absorption Bands (cm^{-1}).[a]

[$CoCl_2(aco)_2$]	17 200 s	15 600 ms	13 400 sh
[$CoBr_2(aco)_2$]	16 400 ms	15 300 ms	
[$Co(NCS)_2(aco)_2$]	16 400 ms	10 600 m	
[$CoCl_2(aco)$]	15 000 w		
[$Co(NO_3)_2(aco)_2$]	18 200 w	15 400 w	
[$Ni(NCS)_2(aco)$]	15 000 m	13 000 sh	8 800 mw

[a] s (strong), m (medium), w (weak) indicate band intensity relative to c.t. background. Peaks marked 's' are clearly visible above background, those marked 'w' are only just distinguishable. sh = shoulder.

and [$NiBr_2(aco)$] and therefore appear to be associated with metal–oxygen modes. In general, we would expect metal–ligand frequencies to be lower in octahedral than in tetrahedral complexes, and for bridging than for terminal ligands.[13] Accordingly, we conclude that the complexes are six-co-ordinate with all the ligands (aco and anions) functioning as bridging groups. The thiocyanato complex [$Ni(NCS)_2(aco)$] has C–N stretching frequencies in the characteristic 'bridging thiocyanate' region.[14] The 1:2 complex [$Mn(NCS)_2(aco)_2$] contains terminal, N-bonded thiocyanate (ν C–N = 2060 cm^{-1}): in this case a six-coordinate configuration will be achieved using only the aco ligands as bridging groups.

The three nitrato complexes all contain co-ordinated nitrate (i.r. data).[16] The cobalt complex has no *d–d* bands above the c.t. background and is presumably six-co-ordinate. The related complex [$Co(NO_3)_2(pyo)_2$] has a six-co-ordinate structure with bridging pyridine N-oxide and monodentate nitrate,[17] but it is not possible to distinguish between the various structural alternatives for the acridine N-oxide complexes using i.r. data alone.

Many (but not all)[18,19] 1:1 mercury(II) halide complexes have dimeric halogen-bridged or ligand-bridged[18] structures. The i.r. spectrum of [$HgCl_2(aco)$] has one strong metal–ligand band (at 340 cm^{-1}) above 250 cm^{-1}. If we assume[20,21] that the Hg–O vibrations occur below 250 cm^{-1}, we can tentatively assign the 340 cm^{-1} band to the terminal Hg–Cl stretch in a chlorine-bridged [$HgCl_2(aco)$]$_2$ dimer. The corresponding pyridine N-oxide complex [$HgCl_2(pyo)$] has three metal–ligand bands between 340–250 cm^{-1} and has been the subject of considerable discussion.[21–25] In this case there is almost certainly extensive mixing of the Hg–O and Hg–Cl modes: the acridine N-oxide complex appears to be much simpler but any suggestions as to its structure must be treated with caution.

All of our acridine N-oxide complexes have 1:1 or 1:2 metal:ligand stoichiometry and none of them contain co-ordinated water or solvent molecules. Pyridine N-oxide or quinoline N-oxide in similar systems, yield a very much wider range of products, including 1:6 and 1:4 complexes (*e.g.* [$Co(pyo)_6$][$CoCl_4$][5], [$Co(pyo)_4(NCS)_2$][8]) and numerous hydrated or solvated compounds (*e.g.* [$Ni(qno)_3(NO_3)_2\cdot{}^1/_2H_2O$],[26] [$Co(pyo)_2(NCS)_2EtOH$][8]).

Electronically, there is very little difference between the three ligands pyridine N-oxide, quinoline N-oxide and acridine N-oxide. Quoted Dq[1] values for the Cr(III) complexes are 1587, 1618 and 1590 cm^{-1} respectively; the visible absorption maxima in the corresponding pairs of tetrahedral complexes [$CoCl_2(qno)_2$] and [$CoCl_2(aco)_2$] or [$CoBr_2(qno)_2$] and [$CoBr_2(aco)_2$] occur at virtually identical frequencies. Experiments with models indicate that octahedral species [$M(aco)_6$]$^{n+}$ will be rather congested around the metal ion, but not to such an extent as to prohibit their formation in all circumstances. Tetragonal [$M(aco)_4X_2$] or tetrahedral [$N(aco)_4$]$^{n+}$ present no serious stereochemical problems. Ragsdale *et al.*[1] have isolated the perchlorates of octahedral [$Cr(aco)_6$]$^{3+}$, tetragonal [$Ni(aco)_4(H_2O)_2$]$^{2+}$ and (probably) tetrahedral [$Co(aco)_4$]$^{2+}$. In our systems, the anions are themselves efficient ligands and are incorporated in the metal co-ordination sphere in preference to additional acridine N-oxide or solvent molecules. Species containing more than two acridine N-oxide molecules per metal ion probably exist in solution but the balance of stability and solubility effects clearly favours the separation of 1:1 and 1:2 complexes much more emphatically than in corresponding reactions with pyridine N-oxide or quinoline N-oxide.

Many of the complexes have oxygen-bridged structures and acridine N-oxide clearly has a marked ability to function as a bridging ligand. The pK$_a$ values for pyridine N-oxide, quinoline N-oxide and acridine N-oxide are 0.79, 0.92 and 1.59, respectively,[12] suggesting that the charge concentration on the oxygen atom, and hence its tendency to form bridged structures, will be greatest in the case of acridine N-oxide. Overcrowding problems may also be alleviated if the ligand bridges between two acceptor atoms.

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