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Metal Complexes of 2-Acetylpyridine N-Oxide Oxime

A. E. LANDERS and D. J. PHILLIPS*

School of Chemistry, The University of New South Wales, Kensington, N.S.W. 2033, Australia

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Complexes of 2-acetylpyridine N-oxide oxime (pxo) are reported with Ni(II), Co(II), Cu(II) and Fe(III). Pxo behaves as an O,N donor via *the N-oxide oxygen and the oxime nitrogen atoms. The complexes M(pxo)Cl_2·CH_3OH (M = Ni, Co) are antiferromagnetic and are thought to be N-oxide-bridged. The temperature dependence of the magnetism of the nickel compound has been compared to that for various models. Complexes of the type M(pxo)$_2X_2$ (M = Ni, Co, Cu) have been obtained, in which X is drawn from Br, NO_3, BF_4 and NCS, depending on the metal; these compounds are all assigned* trans-*$MN_2O_2X_2$ structures. Halogen-bridged structures are proposed for the complexes Cu(pxo)-Hal$_2$ (Hal = Cl, Br). The compound Fe(pxo)Cl_3·*

TABLE I. Analytical Data.

Compound	Analyses % (Calculated and Found)				
	C	H	N	M	
2-Acetylpyridine N-oxide oxime (pxo)	55.3	5.3	18.4	–	white
	55.4	5.4	18.3		
Cu(pxo)Cl_2	29.3	2.8	9.8	22.2	light green
	29.3	2.7	9.8	22.0	
Cu(pxo)Br_2	22.4	2.1	7.5	16.9	light brown
	22.7	2.4	6.9	17.1	
Cu(pxo)$_2$(NO_3)$_2$	34.2	3.3	17.1	12.9	dark green
	34.2	3.5	16.0	13.2	
Cu(pxo)$_2$(BF_4)$_2$[a]	31.1	3.0	10.4	11.7	purple
	31.0	3.0	10.4	11.9	
Ni(pxo)Cl_2·CH_3OH[a]	30.6	3.9	8.9	18.7	green–yellow
	30.3	4.1	8.7	18.5	
Ni(pxo)$_2Br_2$[a]	32.2	3.1	10.7	11.2	light green
	31.9	3.3	10.8	11.5	
Ni(pxo)$_2$(NO_3)$_2$·H_2O[a]	33.3	3.6	16.6	11.6	light green
	35.5	3.7	17.1	11.8	
Ni(pxo)$_2$(NCS)$_2$	40.1	3.4	17.5	12.3	light green
	39.8	3.5	17.7	12.1	
Co(pxo)Cl_2·CH_3OH	30.6	3.9	8.9	18.8	light pink
	30.4	4.0	9.0	18.5	
Co(pxo)$_2Br_2$	32.2	3.1	10.7	11.3	light red
	32.1	3.1	10.9	11.5	
Co(pxo)$_2$(NO_3)$_2$	34.5	3.3	17.3	12.1	dark orange
	34.7	3.5	17.2	12.3	
Co(pxo)$_2$(NCS)$_2$	40.0	3.4	17.5	12.3	light brown
	39.7	3.4	17.2	12.3	
Fe(pxo)Cl_3·CH_3OH[a]	27.7	3.5	8.1	16.1	light yellow
	27.6	4.1	8.0	15.9	

[a] These complexes were prepared as for Ni(pxo)$_2Br_2$, shown in the experimental section. The remaining complexes were obtained using the procedure given for Cu(pxo)$_2$(NO_3)$_2$.

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*Author to whom correspondence should be addressed.

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TABLE II. Ligand Infrared Spectra (cm^{-1}).

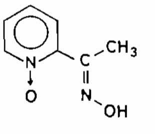
Compound	N-oxide ν(NO)	Oxime ν(NO)	N-oxide δ(NO)
pxo	1218vs, 1211vs	1012vs, 928s	837vs
Cu(pxo)Cl_2	1207vs	1038vs, 976m	848vs
Cu(pxo)Br_2	1208vs	1033s, 971s	844vs
$Cu(pxo)_2(NO_3)_2$	1207vs	1042vs, 978m	848vs
$Cu(pxo)_2(BF_4)_2$	1207s	[a], 972m	857s
Ni(pxo)$Cl_2 \cdot CH_3OH$	1203vs	1035vs, 1008vs, 968vs	839vs
$Ni(pxo)_2Br_2$	1213vs	1042s, 1032s, 1023s, 968vs	845vs
$Ni(pxo)_2(NO_3)_2 \cdot H_2O$	1210m	1047s, 976m	849 m
$Ni(pxo)_2(NCS)_2$	1210vs	1042s, 1021s, 963s	851vs
Co(pxo)$Cl_2 \cdot CH_3OH$	1203vs	1035vs, 1010vs, 965vs	838vs
$Co(pxo)_2Br_2$	1213vs	1042m, 1021vs, 961vs	838vs
$Co(pxo)_2(NO_3)_2$	1202s	1043s, 1022m, 969m	843s
$Co(pxo)_2(NCS)_2$	1203vs	1034s, 1022s, 962s	847vs
Fe(pxo)$Cl_3 \cdot CH_3OH$	1212vs, 1205vs	1042vs, 1018s, 972s	851vs

[a] The oxime ν(NO) band near 1050 cm^{-1} is obscured by tetrafluoroborate absorption.

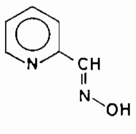
CH_3OH is probably six-coordinate. Magnetic measurements and electronic spectra, to liquid nitrogen temperature, are reported and also infrared spectra, X-ray powder diffraction spectra and Mössbauer spectra.

Introduction

Complexes of pyridine N-oxide and its substituted derivatives have been extensively studied. Many examples of N-oxide-bridged, antiferromagnetic complexes have been reported with copper(II), but very few complexes of this type have been obtained with other transition metal ions [1]. We have been investigating ligands based on pyridine N-oxides, with donor substituents in the 2-position, to see whether antiferromagnetic complexes, with a wider range of transition metals, may be obtained [2–4]. We report complexes of 2-acetylpyridine N-oxide oxime (I, pxo). Antiferromagnetic interaction is found for a nickel(II) and a cobalt(II) complex with this ligand.



(I, pxo)



(II, Hpox)

Part of this work was described in a preliminary communication [2].

TABLE III. Magnetic Data.

Compound	μ_{eff} (B.M.)		θ^a
	298 K	89 K	
Cu(pxo)Cl_2	1.88	1.89	+3
Cu(pxo)Br_2	2.12	2.13	+2
$Cu(pxo)_2(NO_3)_2$	1.87	1.86	0
$Cu(pxo)_2(BF_4)_2$	1.88	1.88	+1
Ni(pxo)$Cl_2 \cdot CH_3OH$	2.93	2.28	-67^b
$Ni(pxo)_2Br_2$	3.16	3.10	−5
$Ni(pxo)_2(NO_3)_2 \cdot H_2O$	3.25	3.15	−4
$Ni(pxo)_2(NCS)_2$	3.18	3.11	−5
Co(pxo)$Cl_2 \cdot CH_3OH$	4.59	3.89	-46^b
$Co(pxo)_2Br_2$	4.77	4.61	−3
$Co(pxo)_2(NO_3)_2$	4.44	4.35	−2
$Co(pxo)_2NCS)_2$	4.54	4.42	−8
Fe(pxo)$Cl_3 \cdot CH_3OH$	6.01	6.09	+7

[a] Curie–Weiss law is taken as $\chi_A^{-1} \propto (T - \theta)$. [b] Deviated from linearity at lower temperatures.

Results and Discussion

Metal complexes are listed in Table I, with analytical data. Mono- or bis-ligand complexes were obtained by reactions in methanol. No tris-ligand, or deprotonated, complexes could be obtained.

Infrared spectra are given in Table II. The spectrum of pxo resembles that of 2-acetylpyridine oxime, with additional infrared bands which we

TABLE IV. Diffuse Reflectance Spectra.

Compound	Temperature (K)	Absorption maxima (cm^{-1} × 10^{-3})			
Ni(pxo)$Cl_2 \cdot CH_3OH$	298	6.0sh,	8.6;	14.6;	[a]
	83	6.6, 8.0,	9.4;	14.9;	[a]
Ni$(pxo)_2Br_2$	298	7.7,	9.1;	14.9;	[a]
	83	7.6,	9.5;	15.5	[a]
Ni$(pxo)_2(NO_3)_2 \cdot H_2O$	298	9.2sh,	11.4;	17.5;	[a]
	83	8.9,	11.8;	17.8	[a]
Ni$(pxo)_2(NCS)_2$	298		10.4	16.9;	[a]
	83	8.8,	11.0;	17.5;	[a]
Co(pxo)$Cl_2 \cdot CH_3OH$	298	6.0,	7.7;	14.7sh,	17.8
	83	6.0,	8.1;		18.0
Co$(pxo)_2Br_2$	298	7.7,		17.8	
	83	7.8,	9.5sh;	18.1	
Co$(pxo)_2(NO_3)_2$	298		10.8;	[a]	
	83	9.2sh,	11.2;	[a]	
Co$(pxo)_2(NCS)_2$	298		9.3;	16.0sh,	19.4
	83	7.2sh,	10.0;	16.0sh,	19.8sh
Cu(pxo)Cl_2	298	11.0sh,	13.6		
Cu(pxo)Br_2	298	11.0sh,	13.8		
Cu$(pxo)_2(NO_3)_2$	298	13.0sh,	17.1		
Cu$(pxo)_2(BF_4)_2$	298	14.8sh,	18.5		
Fe(pxo)$Cl_3 \cdot CH_3OH$	298	8.9,	9.9		

[a] Strong ligand/charge transfer absorption obscures any d–d bands in the 20,000 cm^{-1} region.

assign to pyridyl N-oxide modes. The N-oxide ν(NO) absorption in pxo is a doublet, at 1218, 1211 cm^{-1}, and the δ(NO) band occurs at 837 cm^{-1}. The N-oxide ν(NO) mode decreases, upon coordination, by an average of *ca.* 8 cm^{-1} and δ(NO) increases by *ca.* 9 cm^{-1}. This indicates N-oxide coordination by pxo [1].

With other oxime ligands, the oxime δ(NO) mode has been assigned to a band, or series of bands, in the region 1200–950 cm^{-1} [5–7]. The neutral oxime group always appears to be an N-donor in metal complexes and this causes the oxime ν(NO) band to shift to higher frequency. In 2-pyridinecarboxaldehyde oxime (II, Hpox), ν(NO) occurs at 980 cm^{-1} , and increases by *ca.* 50–90 cm^{-1} upon coordination [5–7]. We have compared the infrared spectra of pxo, 2-acetylpyridine N-oxide, and pyridine N-oxide, in order to detect oxime absorptions in pxo. We assign bands at 1012 and 928 cm^{-1} to the oxime ν(NO) mode in pxo. Both bands rise in frequency on coordination. The 928 cm^{-1} band occurs in complexes at *ca.* 970 cm^{-1} and the 1012 cm^{-1} band is replaced by one to three bands in the range 1047–1010 cm^{-1}, suggesting N-coordination by the oxime group. The oxime ν(CN) mode in pxo is assigned to a band at 1637 cm^{-1}, similar to ν(CN) in other oxime systems [6, 7], but this mode could not be detected in any pxo complexes. In conclusion, therefore, infrared data show that pxo behaves as an O, N ligand, coordinating *via* the N-oxide oxygen and the oxime nitrogen.

Magnetic data, over a temperature range, are given in Table III. The complexes Ni(pxo)$Cl_2 \cdot CH_3OH$ and Co(pxo)$Cl_2 \cdot CH_3OH$ are antiferromagnetic, whereas the remaining complexes are magnetically normal. Diffuse reflectance spectra are listed in Table IV, anion infrared data in Table V, and X-ray powder diffraction patterns, for isostructural complexes, are given in Table VIII.

The nickel complexes have reflectance spectra typical of tetragonally distorted six-coordinate complexes [8]. Bands are present in the 8–10,000 and 14–17,000 cm^{-1} regions, where ν_1 ($^3T_{2g} \leftarrow {}^3A_{2g}$ and ν_2 ($^3T_{1g} \leftarrow {}^3A_{2g}$) of octahedral nickel(II) usually appear. The ν_1 band has shoulders, or resolved components, indicating a lowering of symmetry. The band splittings are more pronounced at liquid nitrogen temperature.

The complex Ni$(pxo)_2(NCS)_2$ has anion infrared absorptions which show that terminal N-bonded thiocyanate is present [9]. The complex, therefore, has an NiN_4O_2 chromophore. A *trans*-N_4O_2 structure is

TABLE V. Infrared Spectra of Anions in Complexes.

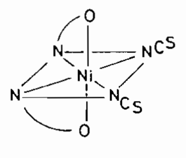
Complex	Anion Absorptions (cm^{-1})			
	ν_3	ν_1	ν_2	ν_4
$Cu(pxo)_2(NO_3)_2$	1412, 1304 vs	[a]	822 m	[a]
$Ni(pxo)_2(NO_3)_2 \cdot H_2O$	1428, 1303 vs	[a]	817 m	722 m
$Co(pxo)_2(NO_3)_2$	1428, 1303 vs	[a]	818 m	[a]
	ν(CN)	ν(CS)		δ(NCS)
$Ni(pxo)_2(NCS)_2$	2094, 2078 vs	806 vw		490 w
$Co(pxo)_2(NCS)_2$	2076 vs	798 sh		[a]
	ν_3	ν_1		ν_4
$Cu(pxo)_2(BF_4)_2$	*ca.* 1080, 1035 vsb	*ca.* 738 sh		519, 524 m

[a] Obscured by ligand absorption.

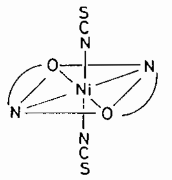
TABLE VI. Magnetic Data for $Ni(pxo)Cl_2 \cdot CH_3OH$ and $Co(pxo)Cl_2 \cdot CH_3OH$.

$Ni(pxo)Cl_2 \cdot CH_3OH$			$Co(pxo)Cl_2 \cdot CH_3OH$		
T(K)	$10^6 \chi'_M$ (cgsu)	μ_{eff}(B.M.)	T(K)	$10^6 \chi'_M$ (cgsu)	μ_{eff}(B.M.)
298	3579	2.93	298	8743	4.59
275	3799	2.90	275	9430	4.57
255	4072	2.89	255	10048	4.55
235	4302	2.85	235	10748	4.51
215	4587	2.82	215	11610	4.49
196	5004	2.81	196	12554	4.45
176	5387	2.77	176	13672	4.41
156	5814	2.71	156	15003	4.35
137	6313	2.64	137	16446	4.26
118	6833	2.57	118	18065	4.14
108	7101	2.49	108	18995	4.07
99	7447	2.43	99	20014	3.99
89	7781	2.36	89	21126	3.89

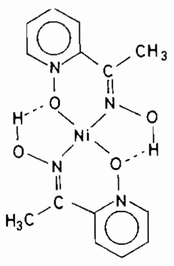
proposed in view of the distortion indicated by the electronic spectrum. Structures (III) or (IV) are possible. The latter structure is preferred, because it incorporates the *trans*-planar arrangement of pxo ligands shown in (V). This maximises hydrogen-bonding by the oxime group. Such hydrogen-bonding is a pronounced feature of oxime complexes, *e.g.* with glyoximes and salicylaldoximes [6]. The anion infrared bands of $Ni(pxo)_2(NO_3)_2 \cdot H_2O$ show that both nitrates are coordinated, and probably unidentate [9–11]. This complex, and $Ni(pxo)_2Br_2$, have reflectance spectra which indicate six-coordinate *trans*-structures, probably of type (IV).



(III)



(IV)



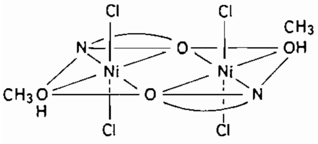
(V)

The mono-ligand complex $Ni(pxo)Cl_2 \cdot CH_3OH$ is antiferromagnetic, and magnetic data are given in Table (VI). The susceptibility data for $Ni(pxo)Cl_2 \cdot CH_3OH$ have been compared with that predicted from various bridged models, using a least-squares procedure, and the best fits are shown in Table VII. The binuclear model gave the closest fit, although several other models gave reasonable fits. The magnetic interaction could be a result of bridging by chloride, oxime or N-oxide. Bridging chloride, in

TABLE VII. Best-Fits of Magnetic Data of $Ni(pxo)Cl_2 \cdot CH_3OH$.[a]

Model	(Reference)[b]	g	J (cm^{-1})	$\Sigma[(\chi_{obs} - \chi_{calc})T]^2$	$\left[\frac{\Sigma(\chi_{obs} - \chi_{calc})^2}{\Sigma(\chi_{obs})^2}\right]^{1/2}$	S.E.[c]
dimer	(12)	2.15	−19.1	0.39×10^{-3}	0.005	0.009
linear trimer	(13)	2.19	−18.2	0.93×10^{-3}	0.010	0.014
equilaterial triangle	(13)	2.20	−13.4	1.06×10^{-3}	0.011	0.015
regular tetrahedron	(14)	2.22	−10.0	1.25×10^{-3}	0.012	0.016
Heisenberg linear polymer	(15)	2.20	−13.5	0.83×10^{-3}	0.009	0.013

[a] Best fits were obtained using a least-squares procedure which minimised $\Sigma[(\chi_{obs} - \chi_{calc})T]^2$. [b] References to the susceptibiity equations are given in parentheses. The temperature independent paramagnetism was taken as 200×10^{-6} cgsu. [c] S.E. is the standard error expression $\{\Sigma[\mu_{eff}(obs) - \mu_{eff}(calc)]^2/(NP - k)\}^{1/2}$, where k is the number of parameters used to fit the NP data points (Ginsberg *et al., Inorg. Chem., 11,* 2884 (1972).



(VI)

complexes of the type NiL_nCl_2, does not usually produce marked interaction [16, 17]. Bridging oxime is well known, and can produce magnetic interaction [6, 18]. We are, however, only aware of bridging with ionised oxime or partially ionised oxime (as in glyoxime complexes) and know of no cases of magnetic interaction produced by neutral oxime groups [6]. Bridging N-oxide is, therefore, considered most likely and a simple binuclear structure is shown in (VI). A polymeric structure could be produced by linking such units *via* chloride bridging.

The complex $Co(pxo)Cl_2 \cdot CH_3OH$ has a reflectance spectrum which indicates a six-coordinate structure [8]. The μ_{eff} decreased by *ca.* 0.7 B.M. between 298 K and 89 K, giving a Weiss *theta* value of −46 K. This is larger than the usual *theta* values for magnetically dilute six-coordinate cobalt(II) (−10 to −40 K) [17, 18]. Magnetic interaction is probably occurring between the cobalt(II) ions. X-ray powder diffraction patterns show that the complex is isostructural with $Ni(pxo)Cl_2 \cdot CH_3OH$.

The reflectance spectra of $Co(pxo)_2Br_2$ and $Co(pxo)_2(NCS)_2$ indicate six-coordinate cobalt(II) [8]. N-bonded thiocyanate is present in $Co(pxo)_2(NCS)_2$, according to the anion infrared absorptions [9]. X-ray powder diffraction spectra show that $Co(pxo)_2Br_2$ is isostructural with $Ni(pxo)_2Br_2$. The cobalt bromide and thiocyanate complexes are assigned *trans*-structures, analogous to (IV).

The infrared spectrum of $Co(pxo)_2(NO_3)_2$ has anion absorptions indicative of coordinated nitrate. The X-ray powder pattern is similar to that of the nickel nitrate complex. A *trans*-CoN_2O_4 structure is, therefore, proposed for $Co(pxo)_2(NO_3)_2$. The reflectance spectrum of $Co(pxo)_2(NO_3)_2$ has a broad band at 10,800 cm^{-1} and also strong absorption occurring above 20,000 cm^{-1}, in which any *d–d* bands are probably obscured by ligand or charge-transfer absorption. The 10,800 cm^{-1} band is unusually high in frequency for ν_1 ($^4T_{2g} \leftarrow {}^4T_{1g}$) of octahedral cobalt(II). The band is in the region for a CoN_6 chromophore, as in $Co(bipy)_3(H_2O)_6SO_4$ which absorbs at 11,000 cm^{-1} [8, 19]. The high frequency of the 10,800 cm^{-1} band may be associated with the low-symmetry of the *trans*-CoN_2O_4 chromophore, although we are not aware of such a spectrum with other tetragonal CoN_2O_4 systems [20, 21]. Some structural distortion might also be responsible for the unusual spectrum. A large distortion would not be expected, in view of the general similarity of the X-ray powder pattern to that of the nickel nitrate complex.

The compound $Cu(pxo)_2(NO_3)_2$ has both nitrate groups coordinated, according to anion infrared absorptions [9]. X-ray powder diffraction spectra show that the complex is isostructural with the nickel and cobalt nitrate complexes. The reflectance spectrum (13,100 sh; 17,100 cm^{-1}) resembles that of $Cu(fomp)_2py_2 \cdot H_2O$ (fomp is 4-formyl-2-methoxyphenolato) which has a CuN_2O_4 chromophore and absorbs at 12,500 and 16,400 cm^{-1} [22]. The infrared spectrum of $Cu(pxo)_2(BF_4)_2$ shows that the anions are coordinated [9]. The reflectance spectrum resembles that of $Cu(pxo)_2(NO_3)_2$, suggesting a similar structure, analogous to (IV).

The copper halide complexes, $Cu(pxo)Hal_2$ (Hal = Cl, Br), are magnetically normal N-oxide bridging, which is very common with 1:1 N-oxide complexes of copper halides, is therefore unlikely [1]. The reflectance spectra have a band at *ca.* 14,000 cm^{-1}. This is too low for a square planar $CuNOHal_2$ struc-

TABLE VIII. Major Lines in X-Ray Powder Diffraction Spectra (*d*-spacings (Å)).

Ni(pxo)Cl$_2$·CH$_3$OH	Co(pxo)Cl$_2$·CH$_3$OH	Ni(pxo)$_2$Br$_2$	Co(pxo)$_2$Br$_2$
8.09s	8.12s	8.36m	8.36m
7.59vs	7.65vs	8.15m	8.22m
–	6.76m	7.30vs	7.30vs
6.12s	6.16s	6.36vs	6.36vs
5.92s	5.99s	5.10m	5.09m
4.28m	4.36m	4.82w	4.80w
4.02m	4.11m	4.08s	4.11s
3.72m	3.75m	3.89m	3.87m
3.60m	3.61m	3.55w	3.58m
3.52s	3.54s	3.51s	3.51s
3.27w	3.30w	3.31w	3.31w
3.11m	3.15m	3.10m	3.10m
3.08m	3.08m	2.92m	2.90m
2.98m	3.01m	2.88m	2.88m
2.95m	2.99m	2.79m	2.80m

Ni(pxo)$_2$(NO$_3$)$_2$·H$_2$O	Co(pxo)$_2$(NO$_3$)$_2$	Cu(pxo)$_2$(NO$_3$)$_2$)
9.25vs	9.16vs	9.40vs
7.22s	7.25s	7.20s
6.64s	6.51s	6.51s
5.69vs	5.57vs	5.63vs
5.31m	5.31m	5.34m
4.86w	5.01w	4.82w
4.78w	4.72w	4.72w
4.22m	4.21m	4.21m
–	3.66w	3.70w
ca. 3.63sh	3.62w	3.65w
–	3.60w	3.60w
3.55s	3.53s	3.54s
3.43m	3.42m	3.41m
3.35w	3.31w	3.28w
3.21s	3.25s	3.22s

ture. For example, the square planar CuN$_2$Cl$_2$ chromophore in Cu(2-methylpyridine)$_2$Cl$_2$ has a band at 17,100 cm^{-1} with a shoulder at 13,900 cm^{-1} [23, 24]. However, the pxo complexes have similar spectra to Cu(en)Cl$_2$ (en = ethylenediamine), which absorbs at 14–15,000 cm^{-1} [25]. Halogen-bridged structures, like that of Cu(en)Cl$_2$, are proposed for the pxo complexes.

The complex Fe(pxo)Cl$_3$·CH$_3$OH is likely to be five or six-coordinate, in view of the structures of iron(III) complexes with other bidentate ligands. The electronic spectrum, with weak absorption *ca.* 10,000 cm^{-1}, resembles the spectra of six- rather than five-coordinate iron(III) complexes [26]. The Mössbauer spectrum has chemical shifts (δ values) of 0.57 and 0.66 mm s^{-1} at room temperature and liquid nitrogen temperatures, respectively (relative to sodium nitroprusside). No detectable quadrupole splitting is present, showing that the fields produced by pxo and chloride are not greatly different. The complex [N(C$_2$H$_5$)$_4$][Fe(phen)Cl$_4$] (phen = 1,10-phenanthroline) has a six-coordinate FeN$_2$Cl$_4$ structure and has a similar spectrum, with δ = 0.65 mm s^{-1} and no quadrupole splitting [27].

Experimental

2-Acetylpyridine N-oxide Oxime (pxo)

Hydroxylamine hydrochloride (20 g) and sodium acetate (40 g) were dissolved in water (60 ml) by warming on a water bath. 2-Acetylpyridine N-oxide [28] (10 g) was dissolved in warm water (20 ml), the two solutions were combined and stirred vigorously and upon allowing to cool a white solid was deposited (7 g). The compound may be recrystallised from a 3:2 alcohol and water mixture.

Complexes of pxo

Complexes were prepared by reacting pxo and the metal salt dissolved in methanol/2,2-dimethoxypropane mixtures. The solutions were either cooled or concentrated and allowed to stand. Typical examples of the preparations are given below, and the procedure which was followed is indicated for each complex in Table I.

$Cu(pxo_2)(NO_3)_2$

A solution of pxo (0.80 g) in warm methanol (30 ml) was added to a warm solution of cupric nitrate trihydrate (1.80 g) in methanol (30 ml) and 2,2-dimethoxypropane (10 ml). The resulting solution was warmed for approximately 10 min and left to stand. After several hours a green powder was deposited.

$Ni(pxo)_2Br_2$

A solution of pxo (0.82 g) in warm methanol (35 ml) was added to a warm solution of nickel(II) bromide trihydrate (1.50 g) in methanol (30 ml) and 2,2-dimethoxypropane (10 ml). The solution was concentrated on a water bath to approximately 25 ml and upon leaving to stand the complex crystallised out.

Analyses and Physical Measurements

These were as previously described [4].

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