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Lanthanide perchlorate complexes of 4-cyano pyridine-N-oxide, 4-chloro 2-picoline-N-oxide and 4-dimethyl amino-2-picoline-N-oxide

N S NAVANEETHAM and S SOUNDARARAJAN*
Department of Inorganic and Physical Chemistry, Indian Institute of Science, Bangalore 560 012, India

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Abstract. Complexes of lanthanide perchlorates with 4-cyano pyridine-1-oxide, 4-chloro 2-picoline-1-oxide and 4-dimethyl-amino 2-picoline-1-oxide have been isolated for the first time and characterized by analysis, conductance, infrared, NMR and electronic spectra. The complexes of 4-cyano pyridine-1-oxides have the composition $Ln(CyPO)_6(ClO_4)_3 \cdot 2H_2O$ (Ln=La, Sm, Dy and Ho); $Ln(CyPO)_7(ClO_4)_3 \cdot 2H_2O$ (Ln = Pr, Nd, Er and Yb); and $Ln(CyPO)_5(ClO_4)_3 \cdot 2H_2O$ (Ln = Gd and Tb). The complexes of 4-chloro 2-picoline-1-oxide analyse for the formulae $Ln(CpicO)_6(ClO_4)_3$ (Ln=La, Pr, Nd and Ho); and $Ln(CpicO)_5(ClO_4)_3$ (Ln=Er and Yb), and those of 4-dimethylamino 2-picoline-1-oxide for $Ln(DMPicO)_6(ClO_4)_3$ (Ln = La and Nd); $Ln(DMPicO)_7(ClO_4)_3$ (Ln=Gd, Er and Yb); and $Ln(DMPicO)_8(ClO_4)_3$ (Ln=Dy and Ho).

Keywords. Lanthanide perchlorates; 4-cyano pyridine-N-oxide; 4-chloro 2-picoline-N-oxide; 4-dimethylamino 2-picoline-N-oxide; proton NMR; electronic spectra.

1. Introduction

The study of the coordination compounds of a variety of lanthanide salts with pyridine N-oxide and methyl substituted analogues have shown that the substitution of methyl group at 3 and 4 positions of pyridine-N-oxide moiety has no influence on the coordination number around the lanthanide ion (Krishna Murthy 1967; Harrison 1970; Koppikar and Soundararajan 1976). However, among the lanthanide perchlorate complexes of 4-nitro, 4-chloro and 4-dimethyl amino pyridine-N-oxides (Navaneetham and Soundararajan 1979a, d), the L:M ratio reduced significantly in the complexes of 4-dimethyl amino pyridine-N-oxide compared to those of pyridine-N-oxide.

Among the disubstituted pyridine-N-oxides, 2,6-dimethyl pyridine-N-oxide (Koppikar and Soundararajan 1975; Karayannis *et al* 1974), 2,4-dimethyl pyridine-N-oxide (Navaneetham and Soundararajan 1979b) and 4-nitro 2-picoline-N-oxides (Navaneetham and Soundararajan 1980) have been used for complexation with lanthanide salts. The steric hindrance due to the methyl groups at 2

* To whom all correspondence should be made.

The unusual coordination number of 5 that has been found in Er^{+3} and Yb^{+3} complexes of CPicO has been found also in the Yb^{+3} complex of tributyl phosphine oxide (Mikulski *et al* 1977). In these complexes of CPicO, the absence of water molecules, coordinated anions, and evidence for bridging ligands, leads to none other than a five coordinate environment around the metal ion.

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Table 5. Proton NMR spectral data for the ligand and their complexes with the diamagnetic La^{+3}-ion (chemical shifts are in τ w.r.t. TMS)

Ligand	Signals for Ligand			Signals for the Complex			Δ in Hz		
	6H	5H	3H	6H	5H	3H	6H	5H	3H
CyPO	8·23 (6,2H)	7·66 (5,3H)		8·72 (6,2H)	7·98 (5,3H)		29 (6,2H)	19 (5,3H)	
CPicO	8·25	7·30	7·47	8·55	7·47	7·65	18	10	11
DMPicO	8·03	6·43	6·50	8·08	6·37	6·43	+3	−4	−4

Further evidence for the coordination of the N-oxide oxygen to the metal ion in the complexes is found from the ^1H NMR spectra of the ligands and their complexes with La^{+3}. A down field shift of αH resonance (table 5), in the diamagnetic complex, compared to that of the ligand, because of the decrease of electron density of the pyridine ring due to complexation, is a consequence of bonding of the N-oxide oxygen to the metal ion. The negative shift of βH signal of DMPicO in the complex indicates shielding of the β-proton which is probably due to the drainage of the electron density from the dimethylamino group to the metal ion on complexation. A similar observation has also been made in the lanthanide complexes of 4-dimethyl-amino pyridine-N-oxide (Navaneetham and Soundararajan 1979d).

The electronic spectra in the visible region, for the Nd^{+3}, Ho^{+3} and Er^{+3} complexes of the ligands reveal that the sharp *f-f* bands exhibit a red shift with respect to aquo ions, due to complexation. The shapes of the hypersensitive $^5G_6 \leftarrow {}^5I_8$ band in Ho^{+3} complexes of CyPO and DMPicO resemble those of eight coordinate complexes studied by Karraker (1967). The shapes of the $^4G_{5/2}$, $^2G_{7/2} \leftarrow {}^4I_{9/2}$ band in Nd^{+3} complexes of CPicO and DMPicO and that of $^5G_6 \leftarrow {}^5I_8$ band in the Ho^{+3} complex of DMPicO are more like those of six coordinate complexes while that of $^2H_{11/2} \leftarrow {}^4I_{5/2}$ band in Er^{+3} complex of DMPicO resembles the shape of seven coordinate complexes reported by Karraker. The hypersensitive $^4G_{5/2}$, $^2G_{7/2} \leftarrow {}^4I_{9/2}$ and $^2H_{11/2} \leftarrow {}^4I_{5/2}$ band shapes in Nd^{+3} and Er^{+3} complexes of CyPO respectively are found to appear like those of the dipicolinic acid (DPA) complexes of lanthanides studied by Jagannathan and Soundararajan (1979), thereby suggesting a nine coordinate geometry around the metal ion in these complexes. The shape of $^2H_{11/2} \leftarrow {}^4I_{5/2}$ band of Er^{+3} complex of CPicO resembles neither those of the complexes studied by Karraker nor those of the DPA complexes.

4. Conclusions

The proton NMR spectra along with the IR data for the complexes indicate the coordination of each of the ligands to the metal ion, through the N-oxide oxygen. The conductivity data for all the complexes coupled with the electronic spectral data for Nd^{+3}, Ho^{+3} and Er^{+3} complexes point to the following coordination numbers in the various complexes.

Complexes	C.N.	+3 metal ion
CyPO complexes	7	Gd and Tb
CyPO complexes	8	La, Sm, Dy and Ho
CyicO complexes	9	Pr, Nd, Er and Yb
CPicO complexes	6	La, Pr, Nd and Ho
CPicO complexes	5	Er and Yb
DMPicO complexes	6	La and Nd
DMPicO complexes	7	Gd, Er and Tb
DMPicO complexes	8	Dy and Ho

Table 4. Important IR bands (cm^{-1}) and their assignments for CPicO and DMPicO complexes.

CPicO	La	Pr	Nd	Ho	Er	Yb	Assignments
1609 m	1614 m	1612 m	1612 m	1612 m	1612 m	1611 m	Ring Stretch
1245 vs	1225 s	1220 s	1220 s	1218 s	1218 s	1215 s	ν_{N-O}
	1075 vs,br	1080 vs,br	1075vs,br	1075 vs,br	1075 vs,br	1070vs,br	ν_3 ClO^-_4
825 m	825 w	825 w	825 w	820 w	820 w	825 w	δ_{N-O}
788 m	790 m	790 m	790 m	790 m	790 w	790 m	γ_{C-H}
	619 m	620 m	621 m	620 m	620 m	620 m	ν_4 ClO^-_4

DMPicO	La	Nd	Gd	Dy	Ho	Er	Yb	Assignments
1630 s	1638 s	1638 s	1640 s	1640 s	1640 s	1640 s	1640 s	Ring Stretch
1205 vs	1220 vs	1215 s	1219 s	1220 s	1220 s	1220 s	1220 s	ν_{N-O}
	1085 vs	1085 vs	1095 vs	1095 vs	1095 vs	1085 vs	1085 vs	ν_4 ClO^-_4
880 m	882 m	882 m	882 m	880 m	880 m	881 m	881 m	δ_{N-O}
785 m	790 m	790 m	792 m	791 m	791 m	790 m	790 m	γ_{C-H}
	622 m	621 m	622 m	622 m	622 m	622 m	622 m	ν_3 ClO^-_4

Abbreviations : vs = very strong, s = strong, m = medium.

Table 3. Important IR bands (cm^{-1}) and their assignments for CyPO complexes.

CyPO	La	Pr	Nd	Sm	Gd	Tb	Dy	Ho	Er	Yb	Assignments
2235 m	2235 m	2235 m	2235 m	2235w	2235 m	2235 m	2235 m	2235 m	2235 m	2235 m	C–N Stretch
1615 m	1620 m	1620 m	1621 m	1620 m	1621 m	1620 m	1620 m	1620 m	1620 m	1620 m	Ring Stretch
1285 s	1290 s	1288 s	1288 s	1288 s	1290 s	1290 s	1288 s	1288 s	1288 s	1290 s	ν_{N-O}
	1270 sh	1270 sh	1270 sh	1271 sh	1270 sh	1270 sh	1270 sh	1270 sh	1270 sh	1270 sh	
	1260 m	1255 sh	1255 sh	1255 sh	1255 sh	1255 m	1255 m	1252 s	1255 m	1255 m	
	1155 s	1155 s	1155 s	1155 s	1155 s	1155 s	1155 s	1155 s	1155 s	1155 s	ν_4 ClO_4
	1095 vs	1095 vs	1095 vs	1095 vs	1095 vs	1095 vs	1095 vs	1095 vs	1095 vs	1095 vs	ν_3 ClO^-_4
1040 m	1040 m	1040 m	1040 m	1040 m	1040 m	1040 m	1040 m	1040 sh	1040 m	1040 m	ν_1 ClO_4 + Ligand
958 w	958 w	960 w	960 w	960 w	960 vw	958 w	960 w	958 w	960 w	960 w	ν_2 ClO_4 + Ligand
860 m	860 m	860 m	860 m	860 m	860 m	860 m	860 m	860 m	860 m	860 m	δ_{N-O}
760 m	765 m	763 m	762 m	765 m	762 w	765 m	765 m	765 m	762 m	762 m	γ_{C-H}
	638 sh	638 m	638 sh	638 sh	638 sh	638 sh	638 sh	638 sh	638 sh	638 sh	ν_3 ClO_4
	627 m	627 m	627 m	627 m	627 m	627 m	627 m	627 m	627 m	627 m	ν_4 ClO^-_4

Abbreviations : vs = very strong, s = strong, m = medium, w = weak, vw = very weak, sh = shoulder.

$Ln(CyPO)_5(ClO_4)_3.2H_2O$ where Ln = Gd and Tb. The complexes of CPicO analyse for the formulae $Ln(CPicO)_6(ClO_4)_3$ where Ln = La, Pr, Nd, and Ho ; and $Ln(CPicO)_5(ClO_4)_3$ where Ln = Er and Yb ; and those of DMPicO for $Ln(DMPicO)(ClO_4)_3$ where Ln = La and Nd ; $Ln(DMPicO)_7(ClO_4)_3$ where Ln = Gd, Er and Yb ; and $Ln(DMPicO)_8(ClO_4)_3$ where Ln = Dy and Ho. All the complexes are soluble in polar solvents such as methanol, acetone, acetonitrile. While DMPicO complexes are soluble in chloroform, the other complexes are insoluble in this solvent. All the complexes are insoluble in nonpolar solvents like benzene and carbon tetrachloride. Molar conductance of the complexes of CPicO and DMPicO are in the range reported for 1 : 3 electrolytes, while those of CyPO are in the range for 1 :1 behaviour (Geary 1971) suggesting thereby that the perchlorate groups are ionic in the former complexes and that two of the three perchlorates are coordinated in the latter.

IR spectral data are presented in tables 3 and 4. Water molecules in the CyPO complexes are lattice held, which is shown by the broad bands in $\sim 3400\,cm^{-1}$ region. In the IR spectra of CyPO complexes, the appearance of two split bands, one in the region 627–638 cm^{-1} and the other in the range 1095–1155 cm^{-1} reveals the presence of coordinated perchlorate groups. Coordinated perchlorate groups (C_{3v}) would result in the appearance of bands at 1158, 10 0, 920 and 648 cm^{-1} in the IR spectra (Hathaway and Underhill 1961 ; Hathaway *et al* 1963). The bands at 1155 cm^{-1} and 638 cm^{-1} are assigned to the ν_4 and ν_3 modes of C_{3v} perchlorate group. The other two bands at 920 cm^{-1} and 1040 cm^{-1} probably merge with the ligand bands occurring in the same regions. The bands at 1095 cm^{-1} and 627 cm^{-1} are assigned to the ν_3 and ν_4 modes of T_d perchlorate group. These aspects of IR spectra pertaining to perchlorate vibrations are in line with the 1 :1 electrolytic behaviour of the CyPO complexes in nitro methane solutions. The ν_{N-O} in CyPO complexes splits into three bands, one strong and two weak bands. The two weak bands appear at lower frequencies than the strong one, compared to the ν_{N-O} of the free ligand. This splitting may be attributed to the presence of two or more inequivalent ligands due to the different environments about the N-O group in the complexes. This seems to be correct in view of the varying coordination numbers around the lanthanide ion and the perchlorate coordination found in these complexes. The γ_{C-H} of CyPO, at 760 cm^{-1}, undergoes a positive shift of 5 cm^{-1} in the complexes indicating the coordination of the ligand to the metal ion.

The IR spectra of the complexes of CPicO and DMPicO reveal two unsplit bands, one in the region 622–627 cm^{-1} and the other in the range 1070–1085 cm^{-1}, assignable to the ν_4 and ν_3 modes of T_d perchlorate group, in conformity with the conductivity evidence of ionic perchlorate groups in these complexes. In the CPicO complexes, the shift of ν_{N-O} towards lower wave numbers indicates the coordination of the ligand to the lanthanide ion through the N-oxide oxygen. The γ_{C-H} vibration of the ligand increases in both CPicO and DMPicO complexes, due to a decrease in the electron density of the pyridine ring, a consequence of binding of the ligand to the metal ion. However, the ν_{N-O} of the ligand shifts to higher frequencies in the complexes of DMPicO. Such an observation has also been made in the case of $(Nb_6Cl_{12})Cl_4(DMPO)_4$ (Field *et al* 1970), where DMPO = 4-dimethylamino pyridine-N-oxide and in the lanthanide complexes of DMPO (Navaneetham and Soundararajan 1979d).

Table 2. Analytical and molar conductance data for CPicO and DMPicO complexes.

Complex	% Metal		% C		% H		% ClO_4		Λ_m^+
	Fd.	Calc.	Fd.	Calc.	Fd.	Calc.	Fd.	Calc.	
$La(CPicO)_6(ClO_4)_3$	10·85	10·70	33·08	33·25	2·69	2·77	22·82	22·97	369·1
$Pr(CPicO)_6(ClO_4)_3$	10·76	10·84	32·96	33·21	2·64	2·77	22·85	22·95	361·7
$Nd(CPicO)_6(ClO_4)_3$	11·19	11·07	33·21	33·13	2·70	2·76	22·76	22·90	366·4
$Ho(CPicO)_6(ClO_4)_3$	12·41	12·45	32·11	32·60	2·62	2·72	22·41	22·53	371·5
$Er(CPicO)_5(ClO_4)_3$	14·08	14·15	29·63	30·40	2·56	2·53	24·93	25·21	405·4
$Yb(CPicO)_5(ClO_4)_3$	14·41	14·54	28·98	30·26	2·58	2·52	24·89	25·08	403·4
$La(DMPicO)_6(ClO_4)_3$	10·44	10·30	42·65	42·67	5·28	5·33	21·96	22·11	349·30
$Nd(DMPicO)_6(ClO_4)_3$	10·52	10·65	42·11	42·51	5·21	5·31	21·89	22·03	351·40
$Gd(DMPicO)_7(ClO_4)_3$	10·22	10·35	43·82	44·22	5·43	5·53	19·32	19·63	356·71
$Dy(DMPicO)_8(ClO_4)_3$	9·86	9·69	45·56	45·81	5·68	5·73	17·65	17·80	345·82
$Ho(DMPicO)_8(ClO_4)_3$	9·95	9·82	45·35	45·75	5·59	5·72	17·69	17·78	346·12
$Er(DMPicO)_7(ClO_4)_3$	10·93	11·10	43·69	43·91	5·38	5·49	19·28	19·50	359·53
$Yb(DMPicO)_7(ClO_4)_3$	11·29	11·27	43·61	43·78	5·31	5·47	19·14	19·45	360·01

+ Molar conductance in acetonitrile : $ohms^{-1}$ cm^2 $mole^{-1}$.

Table 1. Analytical and molar conductance data for CyPO complexes.

Complex	% Metal		%C		%H		$\%ClO_4$		Λ_m^+
	Fd.	Calc.	Fd.	Calc.	Fd.	Calc.	Fd.	Calc.	
$La(CyPO)_6(ClO_4)_3 \cdot 2H_2O$	11·82	11·64	36·29	36·18	2·29	2·35	24·72	24·99	83·24
$Pr(CyPO)_7(ClO_4)_3 \cdot 2H_2O$	10·73	10·68	37·91	38·30	2·39	2·43	22·84	22·68	83·83
$Nd(CyPO)_7(ClO_4)_3 \cdot 2H_2O$	10·89	10·93	37·80	38·18	2·33	2·42	22·82	22·60	85·45
$Sm(CyPO)_6(ClO_4)_3 \cdot 2H_2O$	12·30	12·48	34·98	35·83	2·37	2·32	24·16	24·74	81·42
$Gd(CyPO)_5(ClO_4)_3 \cdot 2H_2O$	14·29	14·41	32·88	32·97	2·14	2·20	26·94	27·32	87·37
$Tb(CyPO)_5(ClO_4)_3 \cdot 2H_2O$	14·72	14·52	32·86	32·71	2·11	2·19	27·01	27·37	86·44
$Dy(CyPO)_6(ClO_4)_3 \cdot 2H_2O$	13·16	13·55	35·82	35·47	2·21	2·23	24·81	24·50	82·31
$Ho(CyPO)_6(ClO_4)_3 \cdot 2H_2O$	13·35	13·52	35·83	35·41	2·34	2·29	23·94	24·45	80·62
$Er(CyPO)_7(ClO_4)_3 \cdot 2H_2O$	12·52	12·45	36·97	37·53	2·22	2·38	22·38	22·21	84·41
$Yb(CyPO)_7(ClO_4)_3 \cdot 2H_2O$	13·01	12·83	36·90	37·39	2·30	2·37	22·04	22·13	84·58

+ Molar Conductance in nitromethane $ohm^{-1}\ cm^2\ mole^{-1}$.

2.5. *Preparation of CPicO complexes*

A solution of hydrated lanthanide perchlorate (1 mM) in ethylacetate (10 ml) was added dropwise, to a solution of CPicO (10 mM) in chloroform (10 ml) with vigorous stirring. The mixture was stirred for about 40 min. The clear liquid above the sticky material was decanted. The sticky substance was washed 3–4 times with hot chloroform to remove excess of the ligand and dissolved in acetone (1 ml). The solution was evaporated to dryness using a high vacuum pump at 80–85° C to get the dry complex.

2.6. *Preparation of DMPicO complexes*

Hydrated lanthanide perchlorate (1 mM) dissolved in ethylacetate (10 ml) was added dropwise to a solution of DMPicO (10 mM) in chloroform (5 ml), with vigorous stirring. The pasty mass, initially formed, changed to a non sticky solid on continuous stirring. The complex was filtered through a sintered crucible, washed 3–4 times with hot ethylacetate to remove traces of the ligand, and finally with a small amount of ether, and dried over phosphorus (V) oxide, in a vacuum desiccator.

2.7. *Analytical methods*

Metal was estimated by EDTA titrations, using xylenolorange as indicator. Perchlorate was determined gravimetrically as nitron perchlorate. All complexes were analysed for carbon and hydrogen by micro analytical methods.

2.8. *Physical methods*

The infrared spectra of CPicO, DMPicO and their complexes, in nujol mull, in the region 400–4000 cm^{-1} were recorded on a Perkin Elmer model-397 spectrophotometer. For CyPO and its complexes, in KBr pellets, the spectra were obtained in the same region on a Carl-Zeiss UR-10 instrument. Proton NMR spectra of CPicO and its La^{+3}-complex were obtained on a Varian T-60 instrument using CH_3CN as solvent and TMS as the internal standard. Spectra for DMPicO and its complex in $CDCl_3$ solutions and for CyPO and its complexes in CH_3NO_2 solutions were also recorded. Electronic spectra for Nd^{+3}, Ho^{+3} complexes of CPicO and DMPicO in CH_3CN solutions and for the complexes of CyPO is CH_3NO_2 solution, were obtained in the region 350–750 nm on a Beckmann model-25 spectrophotometer. The solid state spectra for Nd^{+3}, Ho^{+3} and Er^{+3} complexes of each of the ligands in nujol mull were recorded in the same region on a Unicam SF-700 instrument. Electrolytic conductance measurements for CPicO and DMPicO complexes in CH_3CN solutions and for CyPO complexes in CH_3NO_2 solutions were carried out using a Siemen's conductivity bridge with an immersion type (LTA) cell calibrated with standard KCl solutions.

3. Results and discussion

Analytical and conductivity data are presented in tables 1 and 2. The complexes of CyPO have the compositions $Ln(CyPO)_6(ClO_4)_3.2H_2O$ where Ln = Nd, Sm, Dy and Ho ; $Ln(CyPO)_7(ClO_4)_3 . 2H_2O$ where Ln = Pr, Nd, Er and Yb ; and

and 6 positions of the aromatic ring, at the coordination site around the metal ion, is sufficiently large enough to stabilize complexes with lower L : M ratio, compared to that in the corresponding complexes of pyridine-N-oxide, and 2,4-dimethyl pyridine-N-oxide. However, a lower L : M ratio was found in the complexes of 4-nitro 2-picoline-1-oxide compared to those of 2,4-dimethyl pyridine-N-oxide.

As a part of our studies of adducts of lanthanide salts with 4-substituted and 2,4-disubstituted pyridine-N-oxides with substituents other than methyl group at the 4-position of the aromatic ring, we report in this paper the preparation and characterization of the lanthanide perchlorate complexes of 4-cyano pyridine-N-oxide, 4-chloro 2-picoline-N-oxide and 4-dimethylamino 2-picoline-N-oxide. The isolated complexes have been characterized by analysis, conductance, IR, NMR and electronic spectra.

2. Experimental

2.1. *Materials*

Lanthanide oxides (99·9% pure) were obtained from Indian Rare Earths Ltd., Kerala State. 4-Cyano pyridine-N-oxide (CyPO) (99%) pure was purchased from Aldrich Chemical Co., U.S.A. Hydrated lanthanide perchlorates were obtained as reported earlier (Navaneetham and Soundararajan 1979c).

2.2. *Preparation of 4-chloro 2-picoline-N-oxide (CPicO)*

2-Picoline-N-oxide was obtained by the N-oxidation of 2-picoline as described by Ochiai (1953) for the preparation of pyridine-N-oxide. 4-Nitro 2-picoline-N-oxide was prepared by nitrating 2-picoline-N-oxide by a method similar to that for the preparation of 4-nitro pyridine-N-oxide (Katritzky *et al* 1957); and 4-chloro 2-picoline-N-oxide by the reaction of acetyl chloride with 4-nitro 2-picoline-N-oxide as given by Tetsuzo Kato and Harue Hayshi (1963) (HCl Salt : m.p. 132° Lit. 133·4°).

2.3. *Preparation of 4-dimethylamino 2-picoline-N-oxide (DMPicO)*

This was prepared by reacting dimethylamine with 4-chloro 2-picoline-N-oxide in a sealed tube by a method similar to that for 4-dimethyl-amine pyridine-N-oxide (Katritzky *et al* 1957) [a semi-solid lit. (Agarwal *et al* 1976)].

2.4. *Preparation of CyPO complexes*

Hydrated lanthanide perchlorate (1 mM) dissolved in ethylacetate (10 ml) was added dropwise to a solution of CyPO (10 mM) in chloroform (50 ml), with stirring. Stirring was continued till the precipitation of the complex was complete. The complex was allowed to settle. The supernatant liquid was decanted and the complex washed 4–5 times with hot chloroform. The complex, while still wet with chloroform, was dissolved in A.R. acetone (1 ml) and the solvent then removed using a high vacuum pump at 80–85° C, to get the dry complex.