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PHOSPHINE OXIDE COMPLEXES OF CYCLOPENTADIENYL NEPTUNIUM(IV) AND PLUTONIUM(IV) *N*-THIOCYANATES

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Summary

Phosphine oxide complexes of cyclopentadienyl neptunium(IV) and plutonium(IV) *N*-thiocyanates, $M(cp)(NCS)_3 \cdot xL$ ($cp \equiv \eta^5\text{-}C_5H_5$) ($x = 2$, $M \equiv Pu$, $L \equiv P(CH_3)_3O$ (tmpo); $M \equiv Np$ and Pu, $L \equiv P(CH_3)_2(C_6H_5)O$ (dmppo), $P(CH_3)(C_6H_5)_2O$ (mdppo) and $P(C_6H_5)_3O$ (tppo); $x = 3$, $M = Np$, $L \equiv$ tmpo) and complexes of the tetra-*N*-thiocyanates, $M(NCS)_4 \cdot 4L$ ($M \equiv$ Np and Pu, $L \equiv$ dmppo and mdppo) have been prepared. The IR and near IR–visible spectra of the compounds are reported.

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1. Introduction

Although several phosphine oxide complexes of cyclopentadienyl thorium(IV) [1], uranium(IV) [2, 3], neptunium(IV) [4, 5] and plutonium(IV) [6] trichlorides have been reported, only a few of the analogous actinide(IV) *N*-thiocyanate analogues are known, all of which are uranium(IV) compounds [3, 7]. Bis complexes, $U(cp)(NCS)_3 \cdot 2L$, are formed with the bulky ligands $P(C_6H_5)_3O$ (tppo) and $P\{N(CH_3)_2\}_3O$ (tdpo) [7], whereas tris complexes are formed with the somewhat less bulky ligands $P(CH_3)_2(C_6H_5)O$ (dmppo) and $P(CH_3)(C_6H_5)_2O$ (mdppo) [3]. The attempted isolation of the uranium(IV) complex with the even smaller ligand $P(CH_3)_3O$ (tmpo) was unsuccessful and analogous thorium(IV) complexes could not be obtained [3]. It was therefore of interest to extend this study to the hitherto unknown cyclopentadienyl neptunium(IV) and plutonium(IV) *N*-thiocyanate systems in the expectation that the formation of tris complexes would be less likely with dmppo and mdppo because of the smaller M(IV) radii of neptunium and plutonium as compared with that of uranium(IV), and to prepare the appropriate complexes of the tetra-*N*-thiocyanates, $M(NCS)_4 \cdot 4L$ ($M \equiv$ Np and Pu) as starting materials for the above work.

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2. Experimental details

2.1. *Techniques and materials*

All of the experimental work was carried out in dry atmosphere, nitrogen filled glove-boxes (water, less than 20 ppm, oxygen, not more than 20 ppm) to afford protection against the α radiation emitted by ^{237}Np and ^{239}Pu and to protect samples against atmospheric oxygen and moisture. Cs_2MCl_6 (M ≡ Np and Pu) [8] and the phosphine oxide complexes $PuCl_4\cdot$6tmpo [9], $PuCl_4\cdot$2dmppo and $PuCl_4\cdot$3mdppo [10] were prepared by published methods. Solvents were dried as reported previously [11].

2.2. *Physical measurements*

IR and near IR–visible absorption spectra were obtained as described previously [12].

2.3. *Preparative methods*

(a) $Np(NCS)_4\cdot$4dmppo was prepared by stirring Cs_2NpCl_6 (0.459 g, 0.64 mmol) with dmppo (0.364 g, 2.36 mmol) in boiling methyl cyanide (5 cm^3), effectively forming $NpCl_4\cdot$3.5dmppo, followed by addition of an excess of the ligand (0.098 g, 0.64 mmol) and the stoichiometric amount of potassium thiocyanate (0.249 g, 2.56 mmol). After stirring overnight, the supernatant was vacuum evaporated to dryness and the residue was dissolved in dichloromethane (1 cm^3) from which the green complex precipitated on addition of 2-methylbutane. After washing with 2-methylbutane (2 × 10 cm^3) the product was vacuum dried for 4 h. The yield was only about 20% owing to the difficulty of removing all of the methyl cyanide by evaporation, so that much of the product was left as an oil. The results of analysis showed 21.2% Np and 20.9% NCS. $NpC_{36}H_{44}N_4O_4P_4S_4$ requires 21.8% Np and 21.4% NCS. Yellow-green $Np(NCS)_4\cdot$4mdppo was prepared in the same way. The yield was 78% and the results of analysis showed 17.6% Np and 17.3% NCS. $NpC_{56}H_{52}N_4O_4P_4S_4$ requires 17.8% Np and 17.4% NCS. The known [13] compounds $Np(NCS)_4\cdot$4tmpo, $Np(NCS)_4\cdot$4tppo and $Pu(NCS)_4\cdot$4tppo were also prepared by this method.

(b) $Pu(NCS)_4\cdot$4dmppo was prepared by stirring $PuCl_4\cdot$2dmppo (0.221 g, 0.320 mmol) with the stoichiometric amount of potassium thiocyanate (0.125 g, 1.28 mmol) and an excess of dmppo (0.140 g, 2.83 mmol) in methyl cyanide (10 cm^3) for 16 h. The residue remaining after evaporation to dryness was then treated as in (a). The yield of the brown complex was 65%. The results of analysis showed 22.0% Pu and 21.3% NCS. $PuC_{36}H_{44}N_4O_4P_4S_4$ requires 21.3% Pu and 20.7% NCS. $Pu(NCS)_4\cdot$4mdppo was prepared in the same way from $PuCl_4\cdot$3mdppo. The yield was 94% and the complex was identified by X-ray powder photography; it is isostructural with $Np(NCS)_4\cdot$4mpddo. The known [13] complex $Pu(NCS)_4\cdot$4tmpo was also prepared from $PuCl_4\cdot$6tmpo in this way.

(c) $Np(cp)(NCS)_3\cdot$3tmpo was prepared by treating $Np(NCS)_4\cdot$4tmpo (0.422 g, 0.50 mmol) with the stoichiometric amount of Tl(cp) (0.136 g, 0.50 mmol) in methyl cyanide. After stirring overnight, the supernatant was evaporated to dryness under vacuum and the solid residue was dissolved in dichloromethane (1 cm^3). The solid yellow-orange complex precipitated from this solution on the addition of 2-methylbutane. It was washed with 2-methylbutane (3 × 2 cm^3), then vacuum dried for 4 h. The yield was 68%.

The results of analysis showed 31.2% Np and 23.0% NCS. $NpC_{17}H_{32}N_3O_3P_3S_3$ requires 31.5% Np and 23.1% NCS.

The following complexes were prepared in the same way.

(1) The yield of $Np(cp)(NCS)_3 \cdot 2$dmppo (orange-brown) was 75% and the results of analysis showed 30.0% Np and 21.9% NCS. $NpC_{24}H_{27}N_3O_2P_2S_3$ requires 30.2% Np and 22.2% NCS.

(2) The yield of $Np(cp)(NCS)_3 \cdot 2$mdppo (orange) was 80% and the results of analysis showed 25.5% Np and 18.7% NCS. $NpC_{34}H_{31}N_3O_2P_2S_3$ requires 26.1% Np and 19.2% NCS.

(3) The yield of $Np(cp)(NCS)_3 \cdot 2$tppo (orange-red) was 84% and the results of analysis showed 22.4% Np and 17.0% NCS. $NpC_{44}H_{35}N_3O_2P_2S_3$ requires 23.0% Np and 16.9% NCS.

(4) The yield of $Pu(cp)(NCS)_3 \cdot 2$tmpo (buff brown) was 80% and the results of analysis showed 36.5% Pu and 26.2% NCS. $PuC_{14}H_{23}N_3O_2P_2S_3$ requires 36.1% Pu and 26.3% NCS.

(5) The yield of $Pu(cp)(NCS)_3 \cdot 2$dmppo (red-brown) was 64% and the results of analysis showed 30.0% Pu and 22.0% NCS. $PuC_{24}H_{27}N_3O_2P_2S_3$ requires 30.4% Pu and 22.1% NCS.

(6) The yield of $Pu(cp)(NCS)_3 \cdot 2$mdppo (grey-brown) was 73% and the results of analysis showed 25.4% Pu and 19.0% NCS. $PuC_{34}H_{31}N_3O_2P_2S_3$ requires 26.3% Pu and 19.1% NCS.

(7) The yield of $Pu(cp)(NCS)_3 \cdot 2$tppo (grey-brown) was 76% and the results of analysis showed 23.0% Pu and 16.8% NCS. $PuC_{44}H_{35}N_3O_2P_2S_3$ requires 23.1% Pu and 16.9% NCS.

2.4. *Analytical methods*

The metal analyses were carried out as described previously [8] and by α-counting aliquots of a solution of the complex; thiocyanate was weighed as AgCNS [12].

3. Results and discussion

3.1. *The complexes*

The complexes $M(NCS)_4 \cdot 4L$ (M ≡ Np and Pu, L ≡ dmppo and mdppo), used as starting materials for the main work, were prepared either from Cs_2NpCl_6 by reaction with the ligand in boiling methyl cyanide, followed by the addition of the stoichiometric amount of potassium thiocyanate, or from the chloride complexes $PuCl_4 \cdot xL$ ($x = 2$, L ≡ dmppo and $x = 3$, L ≡ mdppo) by reaction with the stoichiometric amount of potassium thiocyanate. The two routes are essentially the same. The complexes with the cyclopentadienyl actinide(IV) *N*-thiocyanates, $M(cp)(NCS)_3 \cdot xL$ ($x = 2$, $M \equiv$ Pu, $L \equiv$ tmpo, $M \equiv$ Np and Pu, $L \equiv$ dmppo, mdppo and tppo; $x = 3$, $M \equiv$ Np, $L \equiv$ tmpo) were all prepared by treating the complexes $M(NCS)_4 \cdot 4L$

TABLE 1

Principal features in the near IR–visible spectra of the complexes in methyl cyanide solution (1600 - 600 nm)

Complex	*Principal features*[a]
$Np(NCS)_4 \cdot 4$dmppo	710(190.1), 728(130.5), $\underline{742}$(195.8), 775(96.5), 826(87.9), 852(103.5), 904(85.1), 975(178.7), 1553(66.6)
$Np(NCS)_4 \cdot 4$mdppo	708(209.0), 726(152.4), $\underline{741}$(221.3), 774(118.1), 823(103.2), 852(118.1), 904(100.9), 975(189.3), 1555(63.9)
$Np(cp)(NCS)_3 \cdot 3$tmpo	708(56.4), 730(54.3), $\underline{740}$(71.5), 768(42.6), 773(42.3), 808(34.4), 820(37.5), 846(41.2), 903(34.4), 974(67.4), 1550(22.7), 1577(18.6)
$Np(cp)(NCS)_3 \cdot 2$dmppo	708(56.3), 725(54.8), 740(60.9), $\underline{767}$(117.2), 808(71.5), 890(51.7), 974(86.7), 995(70.0), 1567(19.8), 1577(19.0)
$Np(cp)(NCS)_3 \cdot 2$mdppo	702(33.3), 726(39.0), 731sh(58.1), $\underline{766}$(125.7), 810(75.2), 892(56.6), 902sh(39.0), 973(81.8), 1024(34.3), 1567(26.7), 1580(26.2)
$Np(cp)(NCS)_3 \cdot 2$tppo	708(50.4), 729(50.4), 742(56.2), $\underline{767}$(110.0), 811(91.7), 892(50.4), 973(80.2), 980(84.8), 994(64.2), 1024(32.1), 1562(39.0), 1577(37.8)
$Pu(NCS)_4 \cdot 4$dmppo	$\underline{656}$(115.0), 690(75.7), 728sh(58.2), 753(77.1), 771(73.6), 796(58.9), 817(67.3), 886(47.7), 1069(77.1), 1108(74.3)
$Pu(NCS)_4 \cdot 4$mdppo	$\underline{657}$(117.3), 693(78.2), 728(57.0), 753(68.4), 771sh(45.6), 796sh(37.5), 821(62.7), 846(47.2), 1068(78.2), 1140(37.5)
$Pu(NCS)_4 \cdot 4$tppo	$\underline{657}$(110.8), 667sh(100.2), 692(81.0), 726sh(60.8), 744(62.9), 771sh(45.8), 794(74.6), 808sh(57.6), 883(32.0), 1075sh(46.9), 1109(61.8)
$Pu(cp)(NCS)_3 \cdot 2$tmpo	609(21.7), 619(21.8), 654(33.9), 725(24.4), $\underline{762}$(34.6), 783sh(29.1), 805(31.2), 878(16.3), 1063(25.1), 1111(22.0), 1386(10.2), 1578(9.8)
$Pu(cp)(NCS)_3 \cdot 2$dmppo	610(16.1), 618(16.1), 664(18.0), 724(13.7), $\underline{765}$(25.3), 782(20.0), 809(20.1), 882(11.6), 1060(17.3), 1109(15.8), 1387(6.0), 1583(6.6)
$Pu(cp)(NCS)_3 \cdot 2$mdppo	$\underline{611}$(26.1), 668(14.0), 773(14.6), 779sh(14.7), 890(18.1), 911sh(14.7), 1029(17.0), 1110(21.3), 1385(12.5), 1583(14.6)
$Pu(cp)(NCS)_3 \cdot 2$tppo	$\underline{609}$(33.2), 666(20.6), 773(23.3), 801(20.6), 889(19.7), 910sh(15.2), 1025(14.3), 1108(18.3), 1384(13.4), 1578(15.2)

sh, Shoulder.

[a] The strongest band is underlined. Molar extinction coefficients ϵ in parentheses.

with the stoichiometric amount of Tl(cp) in methyl cyanide, followed by vacuum evaporation of the supernatant to dryness and dissolution of the residue in dichloromethane. The complexes precipitated from the resulting solution on the addition of 2-methylbutane.

3.2. Near IR–visible spectra

The spectra (Table 1) of the complexes M(NCS)$_4$·4L (M ≡ Np and Pu, L ≡ dmppo and mdppo; M ≡ Pu, L ≡ tppo) in methyl cyanide solution are very similar to those reported earlier [13] for analogous complexes of the

TABLE 2

IR spectra of the complexes

Complex	$\nu(PO)$ (cm^{-1})	$\Delta\nu(PO)$ (cm^{-1})	$\nu(CN)$ (cm^{-1})	$\nu(M\text{-}C_5H_5)$ (cm^{-1})
Np(NCS)$_4$·4dmppo	1070vs 1056vs	95 109	2051vs	—
Np(NCS)$_4$·4mdppo	1080vs 1065vs	83 98	2088m 2041vs	—
Np(cp)(NCS)$_3$·3tmpo	1095vs, sh 1083vs 1076vs, sh	66 78 85	2049vs	251m
Np(cp)(NCS)$_3$·2dmppo	1081vs 1066s, sh	94 109	2048vs, br	248m
Np(cp)(NCS)$_3$·2mdppo	1083vs 1066s, sh	80 97	2050vs	248m
Np(cp)(NCS)$_3$·2tppo	1072vs, sh 1064vs	118 126	2038vs, br	248m
Pu(NCS)$_4$·4dmppo	1080vs 1065s, sh	85 100	2042vs	—
Pu(NCS)$_4$·4mdppo	1081vs 1069s, sh	82 94	2088m 2060vs, sh 2049vs	—
Pu(NCS)$_4$·4tppo	1081ms 1061ms	109 129	2050vs 2013vs	—
Pu(cp)(NCS)$_3$·2tmpo	1112vs, br	59	2078vs, sh 2058vs	250w
Pu(cp)(NCS)$_3$·2dmppo	1095vs 1088vs 1069s	80 87 106	2040vs	250w
Pu(cp)(NCS)$_3$·2mdppo	1092s 1068m	71 95	2043vs	248m
Pu(cp)(NCS)$_3$·2tppo	1085vs 1070s, sh	105 120	2076s, sh 2050vs	245s

s, Strong; m, medium; w, weak; v, very; sh, shoulder; br, broad.

same stoichiometry and all of them presumably involve eight-coordinate metal centres. The spectra (Table 1) of the complexes Np(cp)$(NCS)_3 \cdot 2L$ in methyl cyanide solution are, in general, quite similar, the most marked differences being the appearance of a band at about 994 nm when L ≡ dmppo and tppo which is absent in the cases of L ≡ mdppo and Np(cp)$(NCS)_3 \cdot$3tmpo and the greater intensity of the band at 740 nm in the spectrum of Np(cp)$(NCS)_3 \cdot$3tmpo as compared with that at 767 nm; in the other three neptunium(IV) complexes the reverse is the case. The spectrum of Np(cp)$(NCS)_3 \cdot$3tmpo in methyl cyanide solution exhibits nine of the bands observed in the spectra of the bis complexes, with three additional medium intensity bands at 773, 820 and 846 nm, a result which may indicate the presence of some Np(cp)$(NCS)_3 \cdot$2tmpo or, possibly, a methyl cyanide solvate in the solution. The spectra of the plutonium(IV) complexes, Pu(cp)$(NCS)_3 \cdot 2L$ with the most bulky ligands mdppo and tppo are almost identical with those with tmpo and dmppo, the most noticeable differences being the absence of bands at 618 and 724 nm and the presence of a new band at 910 nm in the spectra of the former. None of the spectra exhibited bands attributable to $M(cp)_3(NCS)$ (M ≡ Np or Pu) which might be formed by disproportionation.

3.3. *IR spectra*

In the IR spectra of the complexes (Table 2), the shifts in ν(PO) of the ligand on complexation are similar in magnitude to those observed in the spectra of the corresponding complexes $MCl_4 \cdot xL$ (M ≡ Np, Pu [10]) and M(cp)$Cl_3 \cdot xL$ (M ≡ Np [5], Pu [6]); this feature showed a marked degree of splitting in all of the spectra except that of Pu(cp)$(NCS)_3 \cdot$2tmpo. Features due to ν(CN) appeared between 2038 and 2088 cm^{-1}, which is consistent with nitrogen bonding of the thiocyanate group [14], and the relatively high intensities of this mode also suggest nitrogen bonded thiocyanate [15, 16]. The C–S mode in the IR spectra of nitrogen bonded thiocyanate usually appears at 760 - 880 cm^{-1}, compared with 700 cm^{-1} in the case of sulphur bonded thiocyanate [17, 18], but could not be identified owing to interference from modes arising from the organic ligands. The metal–ring mode appeared at 245 - 251 cm^{-1} in the spectra of the cyclopentadienyl compounds, close to the frequencies reported for the analogous chloride complexes, M(cp)$Cl_3 \cdot xL$ (M ≡ Np [5], Pu [6]).

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