Inorganica Chimica Acta, 35 (1979) L309–L311
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Preparation and Resolution of Tris(2,2′-bipyridine) and Tris(1,10-phenanthroline) Complexes of Cr(III)

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Received March 14, 1979

The α-diimine ligands 2,2′-bipyridine and 1,10-phenanthroline have been extensively employed in studies of the thermal behaviour of transition metal (TM) complexes. Present indications suggest an even more prominent role for compounds of these ligands in TM photochemistry. For example, the species Mbipy$_3^{2+}$ (where M = Ru(II), Os(II), Ir(III)) are particularly versatile as both electron and energy transfer donors [1]. More recently, utilization of the Cr(III) compound Crbipy$_3^{3+}$ for solar energy storage has been suggested [2], while several reports have appeared on its general photochemical reactivity [3] and that of the corresponding phenanthroline complex [4]. In the case of Crphen$_3^{3+}$ such studies have been facilitated by the use of optically active samples [4].

In this communication we give details of synthetic procedures for both racemic and optically active Crbipy$_3^{3+}$ and Crphen$_3^{3+}$. Although several synthetic routes to racemic Crbipy$_3^{3+}$ have been reported previously, these generally are unnecessarily cumbersome and involve prior isolation of a simple Cr(II) salt (*e.g.* $CrBr_2$) [5, 6]. Furthermore, in our experience yields by these methods are often unsatisfactory. In contrast we have found a modified version of the preparation described by Baker and Mehta [7] to be relatively simple and very reliable. A complete resolution of Crbipy$_3^{3+}$ into mirror image isomers is as yet unreported, due in part to the high solubility of Crbipy$_3^{3+}$ salts. Thus methods previously successful for Mphen$_3^{3+}$ (M = Cr(III), Co(III)) [8] and Cobipy$_3^{3+}$ [9] do not result in solid diastereoisomer formation for Crbipy$_3^{3+}$. The isolation of solid hexafluorophosphate salts of both isomers is described herein, using $(+)_D$-tris(*l*-cysu)cobaltate(III) as the anionic resolving agent (where cysu = cysteinesulfinato(2$^-$)SN). For the case of Crphen$_3^{3+}$, the literature reference to the racemic complex [10] again requires prior isolation of a simple Cr(II) slat. We offer here a more convenient high yield route similar to that suggested for the bipyridine analog. An excellent procedure for Crphen$_3^{3+}$ is already available [8].

Experimental

Electronic absorption and emission spectra were recorded on a Cary 118C spectrophotometer and a modified Aminco Bowman spectrofluorimeter (Model 4-8203D), respectively. Optical rotation data were obtained on a Bendix polarimeter (Model 1144) with a digital readout to ±0.001°. A Jasco ORD/UV-5/CD-1 spectropolarimeter was employed for CD spectral measurements. Elemental analyses were performed by Midwest Microlabs.

Tris-(2,2′-bipyridine)Chromium(III) Perchlorate

$CrCl_3 \cdot 6H_2O$ (2.67 g) was dissolved in 50 ml 0.1 *M* $HClO_4$ and reduced to Cr(II) over Zn amalgam in a N_2 atmosphere. The Cr(II) solution (30 ml, 0.006 mol) was transferred to a N_2 purged suspension of 2,2′-bipyridine (4.6 g, 0.0295 mol) in 200 ml of 0.01 *M* $HClO_4$ containing 55 g of $NaClO_4$. Although a greyish-black product precipitated immediately, the solution was swirled for a further 10 minutes before air was bubbled through the suspension for three hours. The greyish-yellow residue was then filtered off, washed with ethanol, and the filtrate discarded. The residue was next added to 75 ml of 1 *M* $HClO_4$, magnetically stirred for 10 minutes, and filtered. The yellow solid was redissolved in a minimum volume of water (65 C), and reprecipitated by the addition of solid $NaClO_4$. The final product was filtered, washed with 10 ml of 90% ethanol, 20 ml of ethanol, 40 ml of ether, and sucked dry. Yield of $[Crbipy)_3](ClO_4)_3$ 2.1 g; 42% based on $CrCl_3 \cdot 6H_2O$. The electronic absorption and emission spectra matched very closely those reported in the literature [3, 4, 11].

$(+)_D$ and $(-)_D$-Tris(2,2′-bipyridine)Chromium(III) Hexafluorophosphate

A 40 ml solution of racemic $[Crbipy_3]Cl_3$ was prepared by dissolving the perchlorate salt (1.00 g, 0.0012 mol) in 25 ml water at 50 °C, passing through an anion exchange resin (Dowex 1-X8, Cl^- form), and eluting with water. To this solution was added $(+)_D$-$K_3[Cocysu_3]$ (0.442 g, 0.0006 mol) [12] in 25 ml water. The yellow diastereoisomer $(+)_D[Crbipy_3]$-$(+)_D[Cocysu_3]$ precipitated immediately and after cooling in ice for 10 minutes was collected and washed with 95% ethanol and ether (yield 0.61 g, 99%).

The filtrate was passed through the Cl^- exchange resin to remove any unprecipitated resolving agent, and a solution of NH_4PF_6 (1.0 g in 3 ml water) was added to the eluate. This yielded 0.56 g (96%) of yellow levo product $(-)_D$-$[Crbipy_3](PF_6)_3 \cdot H_2O$ ($[\alpha]_D = -225°$). Found: C 37.78, H 2.69, N 8.88, P 9.63. Calcd. for $C_{30}H_{26}F_{18}P_3N_6Cr$: C 37.01, H 2.69, N 8.63, P 9.55%. The product was further optically

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purified by suspending in 40 ml of water at 40 °C and filtering off the undissolved material (0.25 g, $[\alpha]_D = -82°$). A second more active fraction was obtained by adding NH_4PF_6 to the filtrate (0.20 g, $[\alpha]_D = -440°$).

The diastereoisomer was suspended in 700 ml water at 40 °C and the solution filtered. The filtrate was run through an anion exchange resin to remove the resolving agent, and NH_4PF_6 (2.0 g in 5 ml of water) was added to the eluate. The yellow dextro product $(+)_D$-$[Crbipy_3](PF_6)_3 \cdot H_2O$ precipitated immediately (0.38 g, $[\alpha]_D = +450°$). Found: C 36.77, H 2.48, N 8.49, P 9.60. Calcd. for $C_{30}H_{26}F_{18}P_3N_6Cr$: C 37.01, H 2.69, N 8.63, P 9.55%. Additional, less active, dextro product was obtained by suspending the small amount of previously undissolved diastereoisomer in 700 ml water at 40 °C, and treating the solution as described above (yield 0.14 g, $[\alpha]_D = +330°$).

Tris-(1,10-phenanthroline)Chromium(III) Perchlorate

A 40 ml ethanol solution of 1,10-phenanthroline (5.08 g, 0.0256 mol) was added to 30 g NH_4ClO_4 in 140 ml of 0.01 *M* $HClO_4$, and the mixture purged with N_2. A Cr(II) solution (*vide supra*, 30 ml, 0.006 mol) was then added, resulting in the immediate precipitation of olive-green $[Crphen_3](ClO_4)_2$. The system was maintained under N_2 for a further 10 minutes, and then bubbled with air for three hours. The yellow product was filtered and washed with 90% ethanol, ethanol, then ether. An extraction into 600 ml water (85 °C) followed by addition of solid $NaClO_4$, yielded 3.3 g of $[Crphen_3](ClO_4)_3$ product (60%, based on $CrCl_3 \cdot 6H_2O$). The absorption and emission spectra again agreed very closely with literature data [3, 4, 10].

Results and Discussion

The syntheses outlined for the racemic complexes are to be recommended for their simplicity and reliably high yields. Although the procedure for Crbipy$_3^{3+}$ is similar to that described by Baker and Mehta [7], it differs in two important respects. In the present method, $NaClO_4$ is added to the original 2,2′-bipyridine solution to enhance precipitation of the precursor complex $[Crbipy_3](ClO_4)_2$. Furthermore, after bubbling with air the residue is suspended in 1 *M* $HClO_4$ prior to isolation of the final product. We find yields are often very poor of this step is omitted and the crude product recrystallized directly from water.

An incomplete resolution of Crbipy$_3^{3+}$ has been briefly outlined by Mason and Peart [13] using $(-)_D$-barium tris(catechyl)arsenate(V) as resolving agent. Mixed solvents were necessary and tedious fractional precipitation of the diastereoisomer was involved. No solid products were obtained and the CD spectrum reported was that of the dextro isomer in the presence of racemized resolving agent. The resolution reported herein suffers from none of these deficiencies, and further extends the utility of $(+)_D$-Cocysu$_3^{3-}$ as a general resolving agent for 3+ ctionic species [12]. The success of the resolution is indicated by the excellent mirror image relationship of the CD spectra for the PF_6 salts of the dextro and levo enantiomers (Fig. 1).

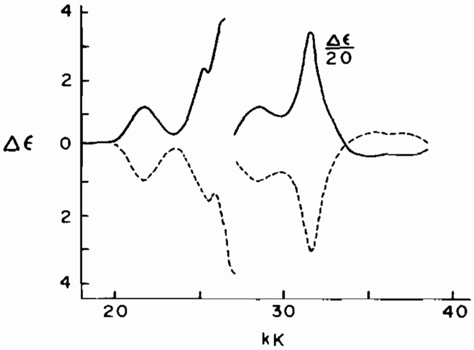

Fig. 1. Circular dichroism spectra in aqueous solution for $(+)_D$-$[Crbipy_3](PF_6)_3$. $[\alpha]_D = +450°$, (——) and $(-)_D$-$[Crbipy_3](PF_6)_3$, $[\alpha]_D = -440°$, (----).

For compounds such as Crbipy$_3^{3+}$ the CD spectra may be used to assign absolute configurations using two independent approaches developed by Mason and co-workers – an empirical method [14] based on the d–d transitions and a non-empirical procedure [13] involving an exciton treatment of the long-axis polarized π–π^* ligand transitions. The two methods correlate well in this instance, with the dextro isomer for example showing the typical CD pattern in the d–d and exciton regions for a species with $\Lambda(C_3)$ absolute configuration. This assignment is supported (though not confirmed) [12] by the observation that $(+)_D$-Crbipy$_3^{3+}$ forms the less soluble diastereoisomer with $(+)_D$-Cocysu$_3^{3-}$. We note that an alternative CD analysis based on the method of Hawkins and co-workers [9] leads to a $\Delta(C_3)$ assignment for $(+)_D$-Crbipy$_3^{3+}$. However, the validity of this latter procedure has been questioned on theoretical grounds [13] and is not supported by recent experimental results for $(+)_D$-Cophen$_3^{3+}$ [15].

Acknowledgements

We gratefully acknowledge support from the NSF-URP program and the Dreyfus Foundation. We thank Dr. John .F. Geldard of Clemson University for assistance with CD measurements.

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