Mixed Thallium(III) Complexes of 2,2′-Dipyridyl Involving Coordinated Perchlorate and Nitrate Ions

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Mixed complex of thallium(III) containing neutral ligands have recently been much discussed.[1-4] We wish to report the infra-red absorption, and the conductivities of solutions in nitrobenzene of the following four white crystalline compounds:

$Tl(dip)_3(ClO_4)_3$ (A) ; $Tl(dip)_2(ClO_4)_3$ (B)
$Tl(dip)_2(NO_3)_3$ (C); $Tl(dip)_2(NO_3)_2ClO_4$ (D

B and C have previously been isolated and were prepared as described in Ref. 2. A and D were prepared from methanol solutions of C. Addition of a large excess of dipyridyl and of sodium perchlorate in methanol gave A, while addition of either one or two equivalents of sodium perchlorate in methanol gave D. All the salts were analysed for Tl, C, H, and N and found to be in agreement with the formulae given.*

The infra-red absorption spectra of Nujol mulls made with polyethylene protected rocksalt discs are given in the figures. A, B, and D show absorption at 625 cm^{-1} attributed to ionic perchlorate, while the large difference around 1100 cm^{-1} between A and B is attributed to overlapping

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* The analyses for the new salts are: A, found, Tl, 20.5; C, 38.29; H, 2.51; N, 8.04. Required for $Tl(dip)_3$, $(ClO_4)_3$, Tl, 20.7; C, 37.1; H, 2.47; N, 8.66.

D, found, Tl, 27.58; C, 32.49; H, 2.29; N, 8.92. Required for $Tl(dip)_2NO_3)_2ClO_4$, Tl, 27.61; C, 32.42; H, 2.16; N, 8.65.

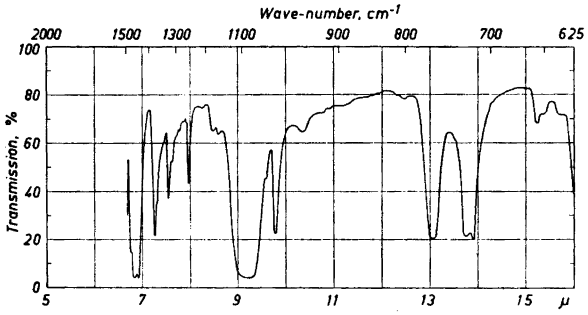

Fig. 1. Infra-red absorption of $Tl(dip)_3(ClO_4)_3$, (A).

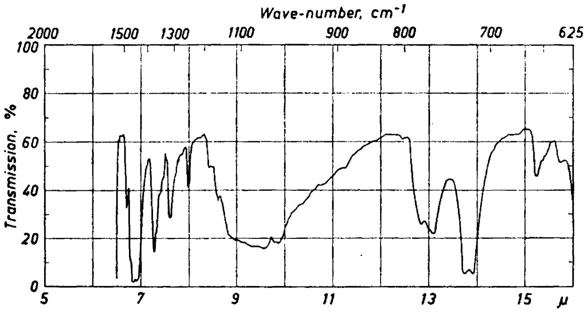

Fig. 2. Infra-red absorption of $Tl(dip)_2(ClO_4)_3$, (B).

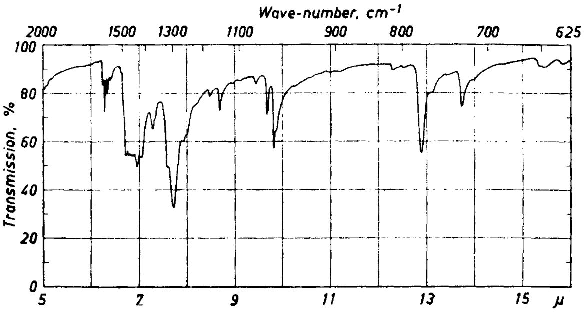

Fig. 3. Infra-red absorption of $Tl(dip)_2(NO_3)_3$, (C).

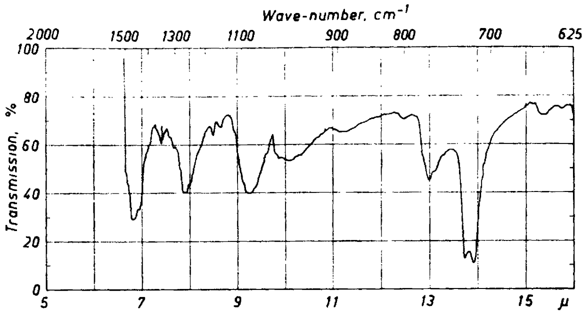

Fig. 4. Infra-red absorption of $Tl(dip)_2(NO_3)_2\ ClO_4$, (D).

absorption of ionic and coordinated perchlorate in the latter.[5,6] The peak at 1370 cm^{-1} observed for C is absent for D and is attributed to ionic nitrate, while the strong absorption in the region 1270—1300 cm^{-1} for both C and D is attributed to coordinated nitrate.[7] The dipyridyl absorption bands typical of metal dipyridyl complexes are present in all cases.[8]

In nitrobenzene A and B are 1:2 electrolytes, C and D are 1:1 electrolytes. The molar conductances (Λ_m) together with those of some similar salts are given in Table 1. The small concentration depend-

Table 1.

Compound	Molar conc. × 10^4	Temp. °C	Λ_m ohm^{-1}
$Tl(dip)_3(ClO_4)_3$ (A)	4.22	22	64.0
$Tl(dip)_2(ClO_4)_3$ (B)	1.02	25	62.5
$[Co(dip)_3](ClO_4)_2$	4.36	25	63.5
$[Cr(dip)_3](ClO_4)_3$	4.36	22	87.8
$[Tl(dip)_2(NO_3)_2]NO_3$ (C)	0.970 to 4.85	25	27.8—27.1
$[Tl(dip)_2(NO_3)_2]ClO_4$ (D)	5.47	22	26.3
$Tl(dip)\ (NO_3)_2ClO_4$	0.514 to 2.14	25	25.8—23.4
$[Rh(dip)_2Cl_2]ClO_4$	4.85	25	28.0

ence of $\Lambda_{\rm m}$ for C over the range given is in accordance with that found for $[Rh(dip)_2Cl_2]ClO_4$.[8] In contrast with this, we found that a salt of composition $Tl(dip)(NO_3)_2ClO_4$ had not only a lower conductance than C and D, but also a strong concentration dependence, as would be expected if extensive ion association had occurred. Because of this difference we conclude that B, C, and D probably all retain two molecules of dipyridyl in nitrobenzene. A and B on solution give species containing one perchlorate ion, while solutions of C and D contain the six coordinate ion $[Tl(dip)_2NO_3)_2]^+$. D is thus analogous to the mixed perchlorate-nitrate complexes of diphenylmethylarsineoxide with cobalt(II), in that, as might have been expected, it is the nitrate which is preferentially coordinated.[6]

None of the compounds reported here are isomorphous.

Conductivity measurements were made with a Radiometer conductivity meter, Type C DM 2d; infrared absorption spectra with a Beckman I.R.8 infrared spectrophotometer.

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The Non-volatile Acids of Succulent Plants Exhibiting a Marked Diurnal Oscillation in their Acid Content

II. Demonstration of Piscidic Acid as one of the Predominating Acids in *Opuntia ficus-indica* L.*

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The present paper represents a new attempt to elucidate the nature of the organic acids found in plants with a typical "crassulacean acid metabolism". In fact, this special form of metabolism was first demonstrated in an *Opuntia* species (in 1804) by the famous Swiss plant physiologist, de Saussure.[1]

The organic acids of a few *Opuntia* species have been investigated by several scientists, but until recently only oxalic, malic, and citric acid had been reported.[2] During screening tests for phorbic acid, carried out in this laboratory in February 1965, it was noticed that an ethyl ester mixture, prepared from the non-volatile acids of *Opuntia ficus-indica* L., produced a dominating peak on the gas chromatogram with a longer retention time than either citric or phorbic acid ethyl ester. In order to carry out a closer investigation of this substance, 15 kg of *Opuntia ficus-indica* L. was supplied from the Canary Islands.

For the investigation we applied mainly the same methods as we had used on earlier occasions for corresponding purposes: [3,4] isolation of the non-volatile acids over their lead salts, esterification of the acid mixtures, fractionation of the ester mixtures in high vacuum, and examination of the individual fractions by various methods, like gas chromatography, investigation of the solid esters by means of classical organic chemical methods,

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* A more extensive survey will be published later in *Meddelelser fra Norsk Farmaceutisk Selskap.*