

869. *2 : 2'-Dipyridyl Complexes of Cobalt, Rhodium, and Iridium.*
Part I. Tervalent Rhodium and Iridium Complexes.

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Tris-2 : 2'-dipyridylrhodium(III) and bis-2 : 2'-dipyridyldichlororhodium(III) perchlorates and nitrates and tris-2 : 2'-dipyridyliridium(III) perchlorate have been prepared. The pure solids are all diamagnetic. Ultraviolet and visible absorption spectra of their aqueous solutions are described.

MANY properties of transition-metal complexes can be accounted for by considering the number of d electrons in the metal ion and their electrostatic interaction with the field provided by the ligands. This "crystal-field" treatment accounts quantitatively for the visible absorption spectra of some complexes of the first transition series^{1,2} and of the second and third transition series.³ The existence of new and intense absorption bands not characteristic of the metal ion or ligand ("charge-transfer" spectra) indicates that in some cases the ligands are not content with the passive rôles ascribed to them in this treatment and has led to a more satisfactory molecular-orbital treatment ("ligand-field")^{4,5} with the crystal-field and Pauling's hybridisation theory as limiting cases.

Chatt's later experimental work⁶ confirmed his suggestion that for complexes containing ligands such as 2 : 2'-dipyridyl which have empty π -type orbitals it is necessary to consider bonds formed from these and filled d orbitals of the metal. These π bonds are formed by the three orbitals whose angular dependence (d_{xy} , d_{xz} , d_{yz}) allows their energy to remain unchanged in the crystal-field treatment of *octahedral* complexes. Octahedral trisdipyridyl complexes with six d electrons may contain three π bonds; tetraco-ordinated square planar complexes two. It is these π bonds, in addition to the σ bonds, which form the "double bonds" suggested by earlier workers⁷ in attempts to explain the anomalously high thermodynamic stability of the diamagnetic trisdipyridyliron(II) cation. The recent

¹ Orgel, *J.*, 1952, 4756.

² Moffitt and Balhausen, *Ann. Rev. Phys. Chem.*, 1956, **7**, 107.

³ Jørgensen, *Acta Chem. Scand.*, 1956, **10**, 500.

⁴ Orgel, *J. Chem. Phys.*, 1955, **23**, 1004, 1819, 1824.

⁵ Owen, *Proc. Roy. Soc.*, 1955, *A*, **227**, 183.

⁶ Chatt, *e.g.*, *J.*, 1955, 4456, and earlier and later papers.

⁷ Burstall and Nyholm, *J.*, 1952, 3570.

preparation⁸ of dipyriddy complexes of chromium and vanadium in low valency states seemed to emphasise the importance of two or even one π bond in such complexes. We therefore surmised that a trisdipyriddy cobalt(II) cation which could contain three π bonds would be stable and later extended our work to rhodium and iridium.

Trisdipyriddy rhodium(III) and trisdipyriddy iridium(III) perchlorate and nitrate were prepared as starting materials for the preparation of similar compounds in lower valency states,⁹ and so that their properties could be compared with those of the trisdipyriddy cobalt(III) cation, whose reduction led to the detection and preparation of the corresponding univalent cobalt complex.¹⁰

Rhodium(III) compounds containing chlorine and dipyriddy have previously been reported¹¹ but only one brown solid, $\text{Rh}(\text{dipy})_3\text{Cl}_3$, has been prepared pure. No dipyriddy iridium compounds have been described.

Published procedures of preparation of trivalent rhodium and iridium salts^{12,13} are all tedious and analytical methods have been either gravimetric determinations of the metal¹⁴ (requiring large amounts of these expensive elements), or based on colour changes which often depend on the composition of the solutions and the time at which measurements were made. These difficulties arise because the starting materials usually rhodium trichloride and potassium chloroiridite) undergo substitutions and redox reactions *slowly* in aqueous solution. We therefore fused the starting materials with the anhydrous ligand, and determined iridium colorimetrically in oxidised solutions which were rapidly equilibrated by addition of platinum black as catalyst.¹⁶

Bisdipyriddy dichlororhodium(III), trisdipyriddy rhodium(III), and trisdipyriddy iridium(III) perchlorates have been isolated. They are all diamagnetic, like the cobaltic complex. The formulæ of the rhodium salts were confirmed by measuring the conductivity in nitrobenzene. These results are compared with those for trisdipyriddy cobalt(II) perchlorate in Fig. 1. The slopes of the plots for the singly, doubly, and triply charged cations are 185, 570, and 1740 respectively. The extrapolated values of the molar conductivity (Λ_0) show the expected¹⁵ proportionality between mobility and cation charge (n), and are given by Λ ($\text{ohm}^{-1} \text{cm}^2$) = $44.8n - 13$. They agree well with those listed (for one concentration) by Harris and Nyholm.¹⁷

The visible and ultraviolet absorption spectra of trisdipyriddy rhodium(III) and -iridium(III) perchlorates in aqueous solution are given, together with those of trisdipyriddy cobalt(III) perchlorate and of 2:2'-dipyriddy in Figs. 2 and 3. The maxima of the absorption bands, their molar extinction coefficients, and the suggested origins of the bands, are given in the Table.

[Co(dipy) ₃](ClO ₄) ₃		[Rh(dipy) ₃](ClO ₄) ₃		[Ir(dipy) ₃](ClO ₄) ₃		Type of band
$\lambda_{\text{max.}}$ (m μ)	$\epsilon_{\text{max.}}$	$\lambda_{\text{max.}}$	$\epsilon_{\text{max.}}$	$\lambda_{\text{max.}}$	$\epsilon_{\text{max.}}$	
Edge at 260	40,000	240	38,800	257	36,400	1
306	34,800	305	33,800	306	27,600	1
317	31,200	318	31,600	315	27,400	1
				~280	~16,400	2
448	67.9	490	27.1			3
		530	28.2			3

These absorption spectra, and those of other dipyriddy complexes,¹⁸ confirm the earlier suggestions¹⁹ that the absorption bands can be divided into three classes, *viz.*, (1) those

⁸ Herzog, *Z. anorg. Chem.*, 1952, **267**, 337; *Naturwiss.*, 1956, **43**, 35.

⁹ Waind and Martin, *Proc. Chem. Soc.*, 1958, 169.

¹⁰ Waind and Martin, International Conference on Co-ordination Chemistry, Rome, 1957.

¹¹ Dwyer, *Chem. Rev.*, 1954, **54**, 1001.

¹² Delépine, see Jørgensen, *Acta Chem. Scand.*, 1957, **11**, 165, for complete references.

¹³ Jaeger and van Dijk, *Proc. Acad. Sci. Amsterdam*, 1934, **37**, 284.

¹⁴ Collman and Holtzclaw, *J. Amer. Chem. Soc.*, 1958, **80**, 2054.

¹⁵ Davies, "Conductivity of Solutions," Chapman and Hall, London, 1933, p. 215.

¹⁶ Waind, *Chem. and Ind.*, 1955, 1388.

¹⁷ Harris and Nyholm, *J.*, 1956, 4377.

¹⁸ Waind and Martin, unpublished work.

¹⁹ *E.g.*, Schlafer, *Z. phys. Chem.*, 1956, **8**, 373.

characteristic of the ligands ($\epsilon \sim 10^4$; ultraviolet), (2) "charge-transfer" or "redox" bands ($\epsilon \sim 10^3$; ultraviolet or visible), and (3) metal ion ("crystal-field") bands ($\epsilon \sim 10^2$; visible or near ultraviolet).

1. *Ligand bands.* These have an irregular vibrational structure indicating strong coupling between electronic and vibrational levels. The highest-energy band of the dipyridyl ligand is displaced to shorter wave-lengths in the order $\text{Rh}^{3+} > \text{Co}^{3+} > \text{Ir}^{3+}$.

FIG. 1. Electrical conductances of (A) $[\text{Rh}(\text{dipy})_2\text{Cl}_2]\text{ClO}_4$, (B) $[\text{Co}(\text{dipy})_3](\text{ClO}_4)_2$, and (C) $[\text{Rh}(\text{dipy})_3](\text{ClO}_4)_3$.

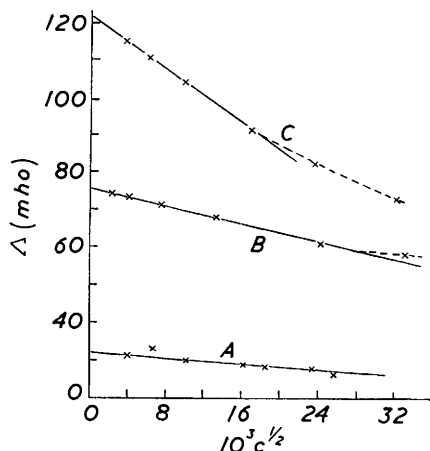


FIG. 2. Ultraviolet spectra of (A) 2:2'-dipyridyl and (B) trisdipyridylcobalt(III), (C) trisdipyridylrhodium(III), and (D) trisdipyridyliridium(III) perchlorates.

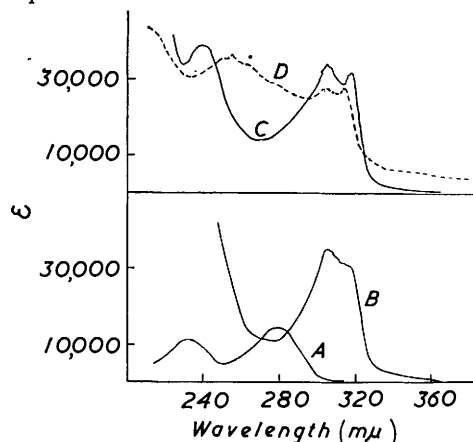
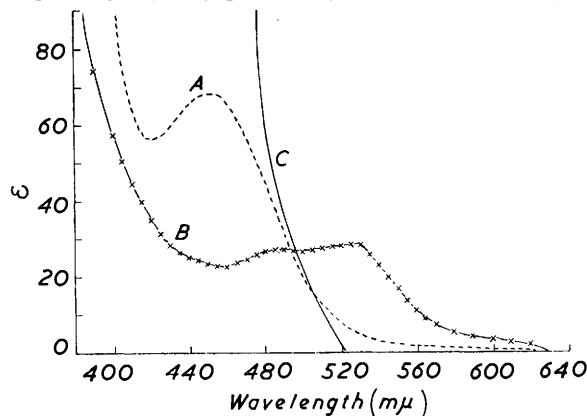


FIG. 3. Visible spectra of (A) $[\text{Co}(\text{dipy})_3]^{3+}$, (B) $[\text{Rh}(\text{dipy})_3]^{3+}$, and (C) $[\text{Ir}(\text{dipy})_3]^{3+}$.



The second, lower-energy band is split; the position of both subsidiary bands is the same for the three triply charged cations. This agrees with Schlafer's results¹⁹ for the corresponding doubly charged cations.

2. *Charge-transfer bands.* The iridium(III) complex differs from the cobalt(III) and rhodium(III) complexes in that it has a broad band in the ultraviolet region, for which $\epsilon \sim 5400$ per dipyridyl molecule (cf. $\epsilon \sim 10,000$ per ligand molecule for bands of type 1). This can presumably be attributed to partial electron-transfer from the iridium to the dipyridyl ligands ($\text{Ir}^{\text{III}} \rightarrow \text{Ir}^{\text{IV}}$) and is exactly analogous to the broad band observed by Jørgensen³ for iridium(III)-pyridine complexes ($\epsilon \sim 2000$ per pyridine molecule compared with $\epsilon \sim 4000$ per pyridine molecule in the ligand bands).

3. *Bands characteristic of the metal ion.* Fig. 3 shows that only the rhodium and cobalt complexes have detectable bands of this type. In both cases they illustrate the surprising success of the crystal-field treatment in predicting the positions and intensities of such bands even when, as here, it can only be an approximation. Thus, for both complexes the bands are broad (t_{2g}^{-1}, e_g) and correspond to those observed³ for the aquo-, halogeno-, and oxalato-complexes and classified according to the crystal-field theory as due to transitions to singlet states. However, the expected difficulty in fitting the dipyriddy ligand into any "spectrochemical series" is well illustrated. Thus, for the other ligands listed the position of the longest-wavelength band has been used successfully to investigate the relative intensities of high crystal-field strengths for the series Co^{3+} , Rh^{3+} , Ir^{3+} . It was found that if the hypsochromic shift for any one ligand was taken as 1.00 for Co^{3+} then the corresponding value for Rh^{3+} was 1.54. For the bands in Fig. 3, if Co^{3+} is taken as unity, the corresponding value for Rh^{3+} is 0.85.

EXPERIMENTAL

All solids were vacuum-desiccated over potassium hydroxide.

Materials.—Rhodium trichloride ($\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$) and potassium chloroiridite ($\text{K}_3\text{IrCl}_6 \cdot 3\text{H}_2\text{O}$) were used as obtained from Messrs. Johnson Matthey and Co. Ltd. All other reagents were "AnalaR."

Tris-2 : 2'-dipyriddyrhodium(III) Perchlorate $[\text{Rh}(\text{dipy})_3](\text{ClO}_4)_3$ and *Dichlorobis-2 : 2'-dipyriddy-dichlororhodium(III) Perchlorate* $[\text{Rh}(\text{dipy})_2\text{Cl}_2](\text{ClO}_4)_3$.—0.20 g. of finely powdered rhodium trichloride trihydrate and 0.78 g. of 2 : 2'-dipyriddy were fused in a test-tube. After expulsion of water the temperature was allowed to rise to the b. p. of dipyriddy (272—273°) and kept thereat for 20 min. during which the reddish-black colour of the rhodium trichloride disappeared leaving a part green, part orange, residue. This was cooled, dissolved in 150 ml. of boiling water, and filtered hot. The filtrate (X) was treated with sodium perchlorate and cooled. The first yellow precipitate (Found: C, 41.65; H, 3.23; N, 10.03; Cl, 12.10; ClO_4 , 17.09; Rh, 17.0%. $[\text{Rh}(\text{dipy})_2\text{Cl}_2]\text{ClO}_4$ requires C, 41.0; H, 2.7; N, 9.55; Cl, 12.08; ClO_4 , 16.96; Rh, 17.54%) was separated pure from the second pink precipitate {Found: C, 41.0; H, 3.14; N, 9.76; ClO_4 , 34.1; Rh, 11.5%. $[\text{Rh}(\text{dipy})_3](\text{ClO}_4)_3$ requires C, 41.4; H, 2.8; N, 9.66; ClO_4 , 34.3; Rh, 11.8%} by repeated fractional crystallisation. Addition of potassium nitrate instead of sodium perchlorate to the hot filtrate (X) gave crystals of $[\text{Rh}(\text{dipy})_2\text{Cl}_2]\text{NO}_3$. The corresponding $[\text{Rh}(\text{dipy})_3](\text{NO}_3)_3$ is very soluble and was not isolated from aqueous solution.

Tris-2 : 2'-dipyriddyiridium(III) Perchlorate $[\text{Ir}(\text{dipy})_3](\text{ClO}_4)_3$.—0.20 g. of potassium chloroiridite and 0.54 g. of 2 : 2'-dipyriddy were heated, then treated as in the preparation of the analogous rhodium complex. The single product was a bright orange powder {Found: C, 36.6; H, 2.5; N, 8.2; ClO_4^- , 31.0; Ir, 20.0%. $[\text{Ir}(\text{dipy})_3](\text{ClO}_4)_3$ requires C, 37.5; H, 2.5; N, 8.76; ClO_4 , 31.1; Ir, 20.12%}.

Tris-2 : 2'-dipyriddy cobalt(III) perchlorate trihydrate $[\text{Co}(\text{dipy})_3](\text{ClO}_4)_3 \cdot 3\text{H}_2\text{O}$ and *tris-*

specific conductance 4.4×10^{-9} mho. All measurements were made at $25^\circ \pm 0.01^\circ$ in a cell with platinised platinum electrodes and the Gambrell A.C. Bridge described by French and Singer.²⁴ The cell constant was 0.115.

Magnetic Measurements.—Susceptibilities were measured by the Gouy method with an air-cooled electromagnet in a flat-bottomed glass tube of 2 mm. internal diameter.

Spectrophotometric Measurements.—All measurements were made at room temperature with a Unicam S.P. 500 spectrophotometer with 1 cm. matched silica cells.

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²⁴ French and Singer, *J.*, 1956, 1424.
