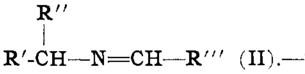
Anal. Calcd. for Ni[$C_{22}H_{18}N_8$]: C, 58.3; H, 4.0; N, 24.7. Found: C, 58.3; H, 4.4; N, 24.1.

Similarly, bis-[1-(2′-pyridyl)-3-(2″-quinolyl)-1,2-diaza-2-propenato]-zinc(II)–0.5-benzene gave the solvent-free complex.

Anal. Calcd. for Zn[$C_{30}H_{22}N_8$]: C, 64.4; H, 4.0. Found: C, 64.2; H, 4.3.

Bis-[2-(2′-pyridyl)-4-(8″-quinolyl)-2,3-diaza-3-butene]-nickel(II) Perchlorate–1-Water.—To a hot solution in dry xylene of bis-[1-(2′-pyridyl)-3-(8″-quinolyl)-1,2-diaza-2-propenato]-nickel(II)–$^1/_3$-benzene was added a slight excess of freshly distilled methyl sulfate. The intense color soon faded and a yellow solid was precipitated. This was collected, washed well with dry ether, and then dissolved in hot aqueous ethanol. Addition of sodium perchlorate in excess led to precipitation of a yellow solid which was recrystallized from aqueous ethanol.

Anal. Calcd. for Ni[$C_{32}H_{28}N_8$](ClO_4)$_2$·H_2O: C, 48.0; H, 3.8; N, 14.0; Cl, 8.9. Found: C, 47.9; H, 4.0; N, 13.8; Cl, 8.8.



Ligands of the Type $R'\text{-}\underset{}{\overset{R''}{\overset{|}{C}}}H\text{—}N\text{=}CH\text{—}R'''$ (II).—The 2-acylpyridines required as starting materials were synthesized by the action of the appropriate Grignard reagents (2 moles) on pure 2-cyanopyridine according to the method of Craig.[17] 2-Pyridyl *n*-amyl ketone (yield 81%, b.p. 134° (12 mm.); **2,4-dinitrophenylhydrazone**, m.p. 124°; *Anal.* Calcd. for $C_{17}H_{19}N_5O_4$: C, 57.1; H, 5.4. Found: C, 57.1; H, 5.4) appears to be new. The ketones were converted to their oximes by warming in aqueous ethanol solution with hydroxylamine hydrochloride and sodium carbonate. Each oxime then was reduced in hot ethanol solution by adding glacial acetic acid and then stirring in zinc dust according to the method of Craig and Hixon.[18] The 2-(α-aminoalkyl) pyridines eventually were recovered as colorless oils by distillation under vacuum. They had characteristic amine-like odors. 1-Amino-1-(2′-pyridyl) ethane, b.p. 100–104° (18 mm.), and 1-amino-1-(2′-pyridyl) propane, b.p. 69° (1 mm.), already have been described by Bower and Ramage.[19]

1-Amino-1-(2′-pyridyl)-butane (b.p. 129–132° (22 mm.), bis-picrate m.p. 202–205°; *Anal.* Calcd. for $C_{21}H_{20}N_8O_{14}$: C, 41.5; H, 3.3. Found: C, 41.5; H, 3.6); **1-amino-1-(2′-pyridyl)-pentane** (b.p. 97–100° (1 mm.), bis-picrate, m.p. 193°; *Anal.* Calcd. for $C_{22}H_{22}N_8O_{14}$: C, 42.5; H, 3.6. Found: C, 42.4; H, 3.7); **1-amino-1-(2′-pyridyl)-hexane** (b.p. 110° (1.5 mm.), oily bis-picrate); and **1-amino-1-(2′-pyridyl)-heptane** (b.p. 118° (1 mm.) oily bis-picrate) appear to be new.

Each of these primary amines was caused to react in hot ethanol with one molecular proportion of pyridine-2-aldehyde, heat being evolved. The resultant Schiff's bases were pale yellow oils which were not further purified but used in the crude condition for coördination with metal perchlorates. Details concerning the complex perchlorates prepared are set out in Table VI.

1,3-Di-(2′-pyridyl)-3-phenyl-2-aza-1-propene (II; R = C_6H_5).—*dl*-Phenyl-(2-pyridyl)-methylamine, b.p. 118–120° (0.6 mm.), was prepared by the Craig and Hixon method[18] in 75% yield. Its **picrate** formed yellow needles, m.p. 198–200° (lit.[9] 181°) (*Anal.* Calcd. for $C_{18}H_{15}N_5O_7$: C, 52.3; H, 3.7; N, 16.9. Found: C, 52.3; H, 3.6; N, 17.0). The **5-bromosalicylidene derivative**, pale yellow prisms from 95% ethanol, had m.p. 132–135° (*Anal.* Calcd. for $C_{19}H_{15}ON_2Br$: C, 62.1; H, 4.1; N, 7.6. Found: C, 61.7; H, 4.1; N, 7.8). Admixture of ethanol solutions of the base (1 mole) and pyridine-2-aldehyde (1 mole) led to evolution of heat and development of a yellow color. The solution was boiled for 1 min., cooled, and allowed to stand. The solid which separated was taken up in *n*-hexane and the solution chilled to −40°. White needles, m.p. 80–81°, separated and were collected.

Anal. Calcd. for $C_{18}H_{15}N_3$: C, 79.1; H, 5.5; N, 15.4. Found: C, 79.0; H, 5.7; N, 15.0.

Copper(II) Coördination Complexes of Type V.—Hot ethanolic solutions of copper(II) chloride (1 mole) and the ligand (2, 3, 4, 5, 6, or 7; 1 mole) were mixed and sodium perchlorate in slight excess was added to the hot solution, which then was allowed to cool. The green complex salt which crystallized was collected and recrystallized from hot water. The melting points recorded in Table VII are virtually decomposition points.

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CONTRIBUTION FROM THE DEPARTMENTS OF CHEMISTRY OF THE UNIVERSITY OF SYDNEY, SYDNEY, AUSTRALIA,
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The Donor Properties of 2,2′-Bipyridine N,N′-Dioxide

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A number of coördination compounds of 2,2′-bipyridine N,N′-dioxide (bipyO_2) with metal salts have been prepared, and their structure determined by analysis, conductivity, and magnetic susceptibility measurements. The compounds were found to be electrolytes, containing the following complex cations: $[M(bipyO_2)_3]^{n+}$ ($M = Cr^{3+}, Mn^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}$), $[Cr(bipyO_2)_2Cl_2]^+$, and $[Cu(bipyO_2)_2]^{2+}$, and the anions ClO_4^- and $PtCl_4^{-2}$.

Introduction

Pyridine N-oxide is known to form coördination compounds with many metal ions and their preparation, properties, and infrared spectra have been reported recently.[1,2] The present paper reports the results of a similar study on the compounds of 2,2′-bipyridine N,N′-dioxide (bipyO_2) with some metals of the first transition series, namely, Cr(III), Mn(II), Fe(III), Co(II), and Ni(II), as well as with Cu(II), Zn(II),

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and Cd(II). In the case of pyridine N-oxide coördination takes place through the oxygen atom and the same was to be expected for bipyO_2. It also could be expected that the presence of two donor oxygen atoms in bipyO_2 would lead to chelation with the metal atom and formation of a seven-membered ring.[3] Although comparatively rare, examples are known of stable complex compounds involving seven-membered chelate rings.[4–8] In fact, provided the ligand can assume a suitable conformation, the formation of such a ring imposes little or no strain on the bond angles of either the ligand or the metal.

Steric considerations suggest that bipyO_2, when acting as a chelating ligand in metal complexes, must assume a staggered (*gauche*) conformation. The use of scale models shows that the chelation about a metal ion requires that the plane of one of the pyridine N-oxide rings is rotated with respect to the other, thus giving rise to a *gauche* conformation, similar to that observed in ethylenediamine–metal complexes.[9,10] It may be mentioned here that a non-planar configuration is also the most likely for uncoördinated bipyO_2 in the solid state, as indicated by our infrared studies to be reported in the following paper. The models also show that, since the ligand molecule is rather compact, it is possible to form tris-chelate octahedrally coördinated complexes. A metal–chelate ring involving a ligand in a *gauche* conformation may assume either of two energetically equivalent enantiomeric configurations.[11] Therefore, in a tris-chelate complex of this type, for each of the two possible enantiomeric orientations of the chelate rings about the metal ion, four different forms are theoretically possible, since each ring may possess either of its enantiomeric configurations.[11] Of these forms, one will have the smallest steric hindrance and so should be energetically favored. The tris-chelate complexes of bipyO_2 are therefore likely to occur only in the two optically isomeric forms corresponding to the lowest energy configurations, although other isomers are theoretically possible.

In agreement with the above considerations it was found, as will be described in detail in the following sections, that bipyO_2 is a good chelating ligand for transition metal ions and readily forms tris-chelate octahedral complexes; but no attempt has so far been made to establish the existence of isomeric forms or to achieve their separation.

Experimental

Starting Materials.—Analytical grade metal salts were used without further purification. **2,2′-Bipyridine N,N-dioxide,** $C_{10}H_8N_2O_2$, was prepared[12] by heating 2,2′-bipyridine (10 g.), glacial acetic acid (75 ml.), and 30% hydrogen peroxide (13 ml.) together at 70–80° for 3 hr. An additional 9 ml. of 30% hydrogen peroxide was added and the temperature maintained at 70–80° for a further 19 hr. On addition of acetone (1 l.), 2,2′-bipyridine N,N′-dioxide precipitated. The material was recrystallized from hot water by the addition of a large excess of acetone, yielding fine white needles, m.p. 297° dec.

Anal. Calcd. for $C_{10}H_8N_2O_2$: C, 63.8; H, 4.3; N, 14.9; O, 17.0. Found: C, 63.5; H, 4.3; N, 14.7; O, 17.1.

Preparation and Characterization of the Complexes.—Conductivity measurements were made at 25° using closed type cells. A low conductivity cell with a cell constant of 0.200_9 cm.$^{-1}$ was used for the solvent, and a medium conductivity cell with a cell constant of 1.30_1 cm.$^{-1}$ was used for the solutions. Since in several cases the conductivity values were observed to vary with time, all measurements were made on freshly prepared solutions, as soon as thermal equilibrium was reached (about 25 min.). The solvents used were N,N-dimethylformamide (DMF) (Eastman White Label), with a specific conductivity of 6.93×10^{-7} ohm^{-1} cm.$^{-1}$ at 25°, and distilled water with a specific conductivity of 1.49×10^{-6} ohm^{-1} cm.$^{-1}$ at 25°. The values of the molar conductivities of the reported complex compounds are listed in Table I.

TABLE I

MOLAR CONDUCTIVITIES OF 2,2′-BIPYRIDINE N,N′-DIOXIDE COMPLEXES AT 25°

Compound, L = bipyO_2	Λ_m, ohm^{-1} cm.^{2} mole^{-1}	Concentration, mmole l.$^{-1}$	Solvent
$[FeL_3](ClO_4)_3 \cdot 3H_2O$	189	1.370	DMF
$[CrL_3](ClO_4)_3 \cdot 2H_2O$	213	0.9537	DMF
$[CrL_2Cl_2](ClO_4) \cdot H_2O$	67.5	1.009	DMF
$[CoL_3](ClO_4)_2 \cdot 2H_2O$	146	1.148	DMF
$[NiL_3](ClO_4)_2 \cdot 2H_2O$	147	1.143	DMF
$[CuL_3](ClO_4)_2 \cdot 2H_2O$	150	1.114	DMF
$[ZnL_3](ClO_4)_2 \cdot 2H_2O$	149	1.083	DMF
$[CdL_3](ClO_4)_2 \cdot 2H_2O$	147	1.150	DMF
$[FeL_3]_2[PtCl_4]_3$	1,090[a]	0.4465	Water
$[MnL_3][PtCl_4]$	266	1.022	Water
$[CoL_3][PtCl_4]$	239	1.068	Water
$[NiL_3][PtCl_4]$	235	1.149	Water
$[CuL_2][PtCl_4] \cdot 4H_2O$	239	1.157	Water
$[ZnL_3][PtCl_4]$	240	1.183	Water

[a] The solution showed signs of hydrolysis.

Magnetic susceptibility measurements were made by the Gouy method on the finely powdered solids at room temperature.[13] The values of the magnetic moments μ_{eff} of the reported compounds, calculated from the magnetic susceptibilities, are listed in Table II.

TABLE II

MAGNETIC MOMENTS OF 2,2′-BIPYRIDINE N,N′-DIOXIDE COMPLEXES

			Spin-free complexes	
Compound L = bipyO_2	Measured susceptibility or χ_m (c.g.s. units)	Obsd. magnetic moments, μ_{eff}	No. of unpaired electrons	Experimental moments, μ_{eff} (B.M.)[13]
$[MnL_3]PtCl_4$	16.49×10^{-3}	6.34	5	5.65–6.10
$[FeL_3](ClO_4)_3 \cdot 3H_2O$	15.43×10^{-3}	6.13	5	5.70–6.0
$[CoL_3](ClO_4)_2 \cdot 2H_2O$	8.97×10^{-3}	4.72	3	4.30–5.20
$[NiL_3](ClO_4)_2 \cdot 2H_2O$	4.00×10^{-3}	3.24	2	2.80–3.50
$[CuL_3](ClO_4)_2 \cdot 2H_2O$	1.419×10^{-3}	2.10	1	1.70–2.20
$[CuL_2]PtCl_4 \cdot 4H_2O$	1.246×10^{-3}	1.99	1	1.70–2.20
$[CuL_2]PtCl_4 \cdot 2H_2O$	1.268×10^{-3}	1.98	1	1.70–2.20
$[CuL_2]PtCl_4$	1.152×10^{-3}	1.90	1	1.70–2.20

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Melting or decomposition temperatures were determined on a Fisher–Johns melting point apparatus.

Thermobalance experiments made use of an automatic recording thermobalance,[14] and were carried out on very finely ground samples (about 0.10 to 0.25 g.).

Preparation of the Perchlorate Complexes, $[M(bipyO_2)_3](ClO_4)_n \cdot yH_2O$.—A hot water solution of the metal perchlorate (hydrated salt) is mixed with a boiling water solution of 2,2′-bipyridine N,N′-dioxide in the molar ratio of 1:3 and the resulting solution then is allowed to cool slowly to room temperature. After standing, the precipitate thus formed is filtered off, washed several times with very small amounts of cold water, recrystallized from boiling water, and dried in air. Unless otherwise stated the compounds are very soluble in boiling water (5 ml. of water dissolves about 0.50 to 1.00 g. of compound), sparingly soluble in cold water, soluble in dimethylformamide, nitromethane, and nitrobenzene, and insoluble in ethanol, methanol, acetone, chloroform, benzene, and tetrahydrofuran. The color, decomposition temperature, and analytical figures for the compounds $[M(bipyO_2)_3](ClO_4)_n \cdot yH_2O$ follow.

Tris-(2,2′-bipyridine N,N′-dioxide)-chromium(III) Perchlorate Dihydrate, $[Cr(C_{10}H_8N_2O_2)_3](ClO_4)_3 \cdot 2H_2O$.—Dark green prisms, m.p. 296–298° dec. To obtain this compound in a pure state the reaction mixture was refluxed for 1 hr.

Anal. Calcd. for $[Cr(C_{10}H_8N_2O_2)_3](ClO_4)_3 \cdot 2H_2O$: Cr, 5.5; C, 37.9; H, 3.0; Cl, 11.2; N, 8.8. Found: Cr, 5.8; C, 37.9; H, 3.1; Cl, 11.0; N, 9.0.

Tris-(2,2′-bipyridine N,N′-dioxide)-manganese (II) Perchlorate Monohydrate, $[Mn(C_{10}H_8N_2O_2)_3](ClO_4)_2 \cdot H_2O$.— Orange needles. The compound decomposes very rapidly to a black powder in the presence of light and less rapidly in the dark. The pure compound was prepared by recrystallizing the crude product from boiling water in the dark. Owing to the great instability of the complex in solution or when finely powdered, conductivity and magnetic susceptibility measurements could not be obtained.

Anal. Calcd. for $[Mn(C_{10}H_8N_2O_2)_3](ClO_4)_2 \cdot H_2O$: Mn, 6.6; C, 43.1; H, 3.1; Cl, 8.5; N, 10.1. Found: Mn, 6.4; C, 43.3; H, 3.3; Cl, 8.7; N, 9.1.

Tris-(2,2′-bipyridine N,N′-dioxide)-iron(III) Perchlorate Trihydrate, $[Fe(C_{10}H_8N_2O_2)_3](ClO_4)_3 \cdot 3H_2O$.—Pale yellow needles, which darken at about 260° but do not melt up to 300°.

Anal. Calcd. for $[Fe(C_{10}H_8N_2O_2)_3](ClO_4)_3 \cdot 3H_2O$: Fe, 5.7; C, 37.0; H, 3.1; Cl, 10.9; N, 8.6. Found: Fe, 5.9; C, 36.7; H, 2.9; Cl, 11.4; N, 8.4.

Tris-(2,2′-bipyridine N,N′-dioxide)-cobalt(II) Perchlorate Dihydrate, $[Co(C_{10}H_8N_2O_2)_3](ClO_4)_2 \cdot 2H_2O$.—Pink-tan needles, stable up to 300°, exploded at about 325°.

Anal. Calcd. for $[Co(C_{10}H_8N_2O_2)_3](ClO_4)_2 \cdot 2H_2O$; Co, 6.9; C, 42.0; H, 3.3; Cl, 8.3; N, 9.8. Found: Co, 6.8; C, 42.5; H, 3.5; Cl, 8.5; N, 8.9.

In a thermobalance experiment, 0.09385 g. (0.109 mmole) of the complex lost 0.00245 g., corresponding to 0.136 mmole of water, between 25 and 100°, and the remaining water was slowly lost, but not completely, up to 300°.

Tris-(2,2′-bipyridine N,N′-dioxide)-nickel(II) Perchlorate Dihydrate, $[Ni(C_{10}H_8N_2O_2)_3](ClO_4]_2 \cdot 2H_2O$.—Yellow-green prisms, stable up to 300°.

Anal. Calcd. for $[Ni(C_{10}H_8N_2O_2)_3](ClO_4)_2 \cdot 2H_2O$: Ni, 6.8; C, 42.0; H, 3.3; Cl, 8.3; N, 9.8. Found: Ni, 6.9; C, 42.7; H, 3.4; Cl, 8.1; N, 9.2.

Tris-(2,2′-bipyridine N,N′-dioxide)-copper(II) Perchlorate Dihydrate, $[Cu(C_{10}H_8N_2O_2)_3](ClO_4)_2 \cdot 2H_2O$.—Light green needles, m.p. 292–294° dec.

Anal. Calcd. for $[Cu(C_{10}H_8N_2O_2)_3](ClO_4)_2 \cdot 2H_2O$: Cu, 7.4; C, 41.8; H, 3.3; Cl, 8.2; N, 9.7. Found: Cu, 7.2; C, 42.3; H, 3.4; Cl, 8.3; N, 9.2.

Tris-(2,2′-bipyridine N,N′-dioxide)-zinc(II) Perchlorate Dihydrate, $[Zn(C_{10}H_8N_2O_2)_3](ClO_4)_2 \cdot 2H_2O$.—White needles stable up to 300°.

Anal. Calcd. for $[Zn(C_{10}H_8N_2O_2)_3](ClO_4)_2 \cdot 2H_2O$: Zn, 7.6; C, 41.7; H, 3.3; Cl, 8.2; N, 9.7. Found: Zn, 7.8; C, 42.4; H, 3.6; Cl, 8.0; N, 9.0.

Tris-(2,2′-bipyridine N,N′-dioxide)-cadmium(II) Perchlorate Monohydrate, $[Cd(C_{10}H_8N_2O_2)_3](ClO_4)_2 \cdot H_2O$.—Ivory needles, stable up to 300°. The compound is much less soluble than the analogous compounds. It could be dissolved in DMF for conductivity measurements upon warming at 50°.

Anal. Calcd. for $[Cd(C_{10}H_8N_2O_2)_3](ClO_4)_2 \cdot H_2O$: Cd, 12.6; C, 40.3; H, 2.9; N, 9.4; Cl, 7.9. Found: Cd, 12.3; C, 40.1; H, 3.1; N, 9.0; Cl, 8.0.

Preparation of the Tetrachloroplatinate Complexes, $[M(bipyO_2)_3]_n[PtCl_4]_m$.—Solid 2,2′-bipyridine N,N′-dioxide was dissolved with stirring in a warm (45°) water solution of the metal chlorides (hydrated salts) in the molar ratio 3:1. After cooling to room temperature, the almost clear solution was filtered and treated slowly with stirring with the required (stoichiometric) amount of a filtered solution of K_2PtCl_4 in water. A precipitate separated, which was filtered off, washed three times with small amounts of cold water and twice with 95% ethanol, and dried *in vacuo* over phosphoric anhydride for 12 hr. The compounds are readily soluble in boiling water, moderately soluble in cold water, and practically insoluble in common organic solvents. The color, decomposition temperature, and analytical figures for the compounds $[M(bipyO_2)_3]_n[PtCl_4]_m$ follow.

Tris-(2,2′-bipyridine N,N′-dioxide)-manganese(II) Tetrachloroplatinate(II), $[Mn(C_{10}H_8N_2O_2)_3][PtCl_4]$.—The preparation was carried out in a darkened room. The yields and purity of the final product were increased by cooling the mother liquor for 1 hr. in a refrigerator. The product was dried over phosphoric anhydride *in vacuo* for 12 hr. in the dark, yielding bright orange prisms which start darkening at 250° but do not melt up to 300°.

Anal. Calcd. for $[Mn(C_{10}H_8N_2O_2)_3][PtCl_4]$: C, 37.7; H, 2.5; Cl, 14.8; N, 8.8. Found: C, 37.5; H, 2.9; Cl, 14.3; N, 8.5.

In the crystalline state, the complex is quite stable to light for about 1 hr., but solutions are far more sensitive and darken within a few minutes.

Tris-(2,2′-bipyridine N,N′-dioxide)-iron(III) Tetrachloroplatinate(II), $[Fe(C_{10}H_8N_2O_2)_3]_2[PtCl_4]_3$.—Small, light tan needles, m.p. 227–229° dec.

Anal. Calcd. for $[Fe(C_{10}H_8N_2O_2)_3]_2[PtCl_4]_3$: C, 32.0; H, 2.2; Cl, 18.9; N, 7.5. Found: C, 32.0; H, 2.0; Cl, 18.4; N, 7.2.

Tris-(2,2′-bipyridine N,N′-dioxide)-cobalt(II) Tetrachloroplatinate(II), $[Co(C_{10}H_8N_2O_2)_3]PtCl_4$.—Short, fine reddish orange needles, stable up to 300°.

Anal. Calcd. for $[Co(C_{10}H_8N_2O_2)_3]PtCl_4$: C, 37.5; H, 2.5; Cl, 14.8; N, 8.8. Found: C, 37.6; H, 2.7; Cl, 14.7; N, 8.8.

Tris-(2,2′-bipyridine N,N′-dioxide)-nickel(II) Tetrachloroplatinate(II), $[Ni(C_{10}H_8N_2O_2)_3]PtCl_4$.—Very fine, gold-yellow needles, stable up to 300°.

Anal. Calcd. for $[Ni(C_{10}H_8N_2O_2)_3]PtCl_4$: C, 37.5; H, 2.5; Cl, 14.8; N, 8.8. Found: C, 37.6; H, 2.5; Cl, 14.7; N, 8.6.

Bis-(2,2′-bipyridine N,N′-dioxide)-copper(II) Tetrachloroplatinate(II) Tetrahydrate, $[Cu(C_{10}H_8N_2O_2)_2]PtCl_4 \cdot 4H_2O$.—The product was dried in air. It exists as small yellow-green needles which turn dark green at about 100°, and dark brown at about 210°, but do not melt up to 300°.

Anal. Calcd. for $[Cu(C_{10}H_8N_2O_2)_2]PtCl_4 \cdot 4H_2O$: C, 28.3; H, 2.9; Cl, 16.7; N, 6.6; H_2O, 8.5. Found: C, 28.1; H, 2.9; Cl, 16.7; N, 6.6; H_2O, 8.1.

In a thermobalance experiment 0.2410 g. (0.284 mmole) of the complex lost 0.01050 g. (corresponding to 0.583 mmole of water) between 36 and 77°, and an equal loss of weight occurred again between 77 and 100°. The intermediate product obtained at 77° corresponds to $[Cu(bipyO_2)_2]PtCl_4 \cdot 2H_2O$. It is a light green crystalline powder, which is stable in air at 45% humidity (26°) and is quantitatively reconverted into the tetrahydrate by

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exposure to air saturated with water at room temperature.

Bis-(2,2'-bipyridine N,N'-dioxide)-copper(II) Tetrachloroplatinate(II), $[Cu(C_{10}H_8N_2O_2)_2]PtCl_4$.—The yellow-green compound, $[Cu(C_{10}H_8N_2O_2)_2]PtCl_4 \cdot 4H_2O$, was dried by heating under reduced pressure in an Abderhalden apparatus for 1 hr. at 110° in the presence of anhydrous magnesium perchlorate as desiccant. Deep olive-green crystals were formed, which on exposure to air at 45% humidity (26°) were transformed in a few hours into the light green dihydrate, and when exposed to water-saturated air, at room temperature, re-formed the yellow-green tetrahydrate.

Anal. Calcd. for $[Cu(C_{10}H_8N_2O_2)_2]PtCl_4$: C, 30.9; H, 2.1; Cl, 18.3; N, 7.2. Found: C, 31.3; H, 2.1; Cl, 17.9; N, 7.3.

Tris-(2,2'-bipyridine N,N'-dioxide)-zinc(II) Tetrachloroplatinate(II), $[Zn(C_{10}H_8N_2O_2)_3]PtCl_4$.—Light tan crystals, which turn to dark red-brown at about 280°, but do not melt up to 300°.

Anal. Calcd. for $[Zn(C_{10}H_8N_2O_2)_3]PtCl_4$: C, 37.3; H, 2.5; Cl, 14.7; N, 8.7. Found: C, 37.0; H, 2.8; Cl, 14.2; N, 8.4.

Dichloro-bis-(2,2'-bipyridine N,N'-dioxide)-chromium(III) Perchlorate Monohydrate, $[Cr(C_{10}H_8N_2O_2)_2Cl_2](ClO_4) \cdot H_2O$.—Finely powdered 2,2'-bipyridine N,N'-dioxide (2.07 g., 11 mmoles) was suspended in a solution of $CrCl_3 \cdot 6H_2O$ (1.33 g., 5 mmoles) in 20 ml. of absolute ethanol, and evaporated to dryness on a water bath. The solid residue then was stirred with 200 ml. of ethanol until all the tarry material was dissolved, leaving a crop of violet crystals. These were filtered off, thoroughly washed with ethanol, and dissolved in 500 ml. of cold water by stirring mechanically for 15 min. The solution was filtered and treated slowly, with stirring, with a solution of $NaClO_4$ (2 g.) in water (100 ml.). A precipitate formed, which was collected, washed thoroughly first with water and then with ethanol, and then dried *in vacuo* for 12 hr. over phosphoric anhydride. Very fine purple crystals, stable up to 300°, were obtained.

Anal. Calcd. for $[Cr(C_{10}H_8N_2O_2)_2Cl_2](ClO_4) \cdot H_2O$: C, 39.0; H, 2.9; Cl, 17.3; N, 9.1. Found: C, 38.7; H, 3.0; Cl, 17.0; N, 8.7.

The compound is practically insoluble in cold water, soluble with decomposition in hot water, soluble in DMF when warmed to about 50°, and insoluble in all common organic solvents. On repeated preparation, the compound always was obtained as the above described very fine purple crystals. No evidence is available to decide which of the two possible *cis–trans* isomers of $[Cr(bipyO_2)Cl_2]^+$ is obtained.

Dichloro-bis-(2,2'-bipyridine N,N'-dioxide)-chromium(III) Tetrachloroplatinate(II), $[Cr(C_{10}H_8N_2O_2)_2Cl_2]_2PtCl_4$.—This was prepared as described for the corresponding perchlorate from $CrCl_3 \cdot 6H_2O$ (0.472 g., 1.78 mmoles), 2,2'-bipyridine N,N'-dioxide (1.0 g., 5.32 mmoles), and K_2PtCl_4 (1.11 g., 2.67 mmoles). Upon standing overnight in a refrigerator the reaction mixture gave a tan-pink precipitate which was filtered off, washed twice with 3 ml. of cold water and twice with 2 ml. of 95% ethanol, and then dried *in vacuo* for 12 hr. over phosphoric anhydride. The compound is hygroscopic and is in the form of very fine tan-pink crystals stable up to 300°.

Anal. Calcd. for $[Cr(C_{10}H_8N_2O_2)_2Cl_2]_2PtCl_4$: C, 36.0; H, 2.4; Cl, 21.2; N, 8.4. Found: C, 35.8; H, 2.6; Cl, 20.6; N, 8.4.

On repeated preparation, the compound always was obtained as the above described very fine tan-pink crystals. No evidence is available to decide which of the two possible *cis–trans* isomers of $[Cr(bipyO_2)_2Cl_2]^+$ is obtained. The compound is insoluble in cold water, soluble with decomposition in hot water (50°), and insoluble in all common organic solvents.

Cadmium Chloride Complex, $Cd(C_{10}H_8N_2O_2)Cl_2$.—The 2,2'-bipyridine N,N'-dioxide (0.5 g., 2.66 mmoles) was dissolved in 5 ml. of hot water and the solution was mixed with a hot solution of $CdCl_2$ (0.486 g., 2.66 mmoles) in 2 ml. of water. Immediately a product separated which after cooling was filtered off and washed six times with 5-ml. portions of water. It exists as off-white needles, stable up to 300°, almost insoluble in water and insoluble in common organic solvents. A sample of the complex showed no loss of weight after drying for 4 hr. at 200° and 5 mm., indicating the absence of water of crystallization.

Anal. Calcd. for $Cd(C_{10}H_8N_2O_2)Cl_2$: Cd, 30.3; C, 32.3; H, 2.2; Cl, 19.1; N, 7.5. Found: Cd, 30.3; C, 32.0; H, 2.5; Cl, 19.0; N, 7.0.

Although the compound is practically insoluble, a 1.152×10^{-3} *M* solution in water could be obtained by shaking the finely powdered solid with water for 4 hr. The conductivity of this solution, however, was much higher than required for a divalent electrolyte such as $[Cd(bipyO_2)_2]CdCl_4$, and indicated almost complete dissociation of the chloride ions.

Results and Discussion

The reaction between $bipyO_2$ and the perchlorates of transition metals, carried out as described in the Experimental section, yields well crystallized products, which on the basis of their analyses and conductivity values can be formulated as the perchlorates of the tris-(2,2'-bipyridine N,N'-dioxide) metal cation, $[M(bipyO_2)_3]^{n+}$ ($M = Cr^{3+}, Mn^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}$). These complex salts generally contain water of crystallization which is retained up to realtively high temperatures. For instance, thermobalance experiments[14] show that $[Co(bipyO_2)_3](ClO_4)_2 \cdot 2H_2O$ still retains one molecule of water at 100°. This is then lost gradually between 100 and about 325°, at which temperature the compound decomposes. In the crystalline state the complex salts $[M(bipyO_2)_3](ClO_4)_n$ are remarkably stable to air and light, with the exception of the Mn(II) compound, which is extremely light-sensitive. In aqueous solution they are somewhat less stable and tend to decompose slowly with separation of hydrolysis products. The crystalline salts have a high thermal stability. Most of them are unaltered up to 300° but at higher temperatures explode; for example, the above-mentioned Co(II) complex explodes violently at about 325°.

When $bipyO_2$ is allowed to react with the transition metal chlorides, in most cases the product is again the tris-chelate cation, $[M(bipyO_2)_3]^{n+}$, which cannot generally be isolated as the extremely soluble chloride salt, but is easily obtained as the sparingly soluble tetrachloroplatinate. The tetrachloroplatinates of the complex cation $[M(bipyO_2)_3]^{n+}$ are strictly analogous in their general properties to the corresponding perchlorates, except that on heating they decompose without exploding and do not contain water of hydration. However, they are somewhat hygroscopic. In a few cases, namely with Cr(III), Cu(II), and Cd(II) chlorides, the reaction with $bipyO_2$ does not yield the tris-chelate cation $[M(bipyO_2)_3]^{n+}$. Cadmium(II) chloride gives an insoluble adduct $Cd(bipyO_2)Cl_2$, the structure of which could not be determined; chromium(III) chloride gives the mono-positive cation $[Cr(bipyO_2)_2Cl_2]^+$, which was isolated as the tetrachloroplatinate. The Cu(II) complex salt crystallizes from water as the tetrahydrate $[Cu(bipyO_2)_2]PtCl_4 \cdot 4H_2O$, which loses two molecules of water between 36 and 77° to give the semi-stable species $[Cu(bipyO_2)_2]PtCl_4 \cdot 2H_2O$, and at 100° is completely transformed into the anhydrous salt $[Cu(bipyO_2)_2]PtCl_4$.

With the exception of the insoluble Cd(bipyO_2)Cl_2 compound, all the other investigated bipyO_2 complexes behave in solution as strong electrolytes. The values of the molar conductivities, Λ_m, in DMF (Table I) are in good agreement with those reported for similar complex salts of pyridine N-oxide under the same conditions[1]: from 85 ohm^{-1} $cm.^2$ $mole^{-1}$ downward for uni-univalent salts, in the range 140–170 ohm^{-1} $cm.^2$ $mole^{-1}$ for di-univalent salts, and in the range 200–260 ohm^{-1} $cm.^2$ $mole^{-1}$ for tri-univalent salts. The molar conductivities in water (Table I) are also in good agreement with the values reported for simple[15] and complex[16] salts: Λ_m = 250 ohm^{-1} $cm.^2$ $mole^{-1}$ (at 0.920 mmole $l.^{-1}$) in water at 25°, for a di-divalent electrolyte such as $[Co(NH_3)_5Cl]C_2O_4$; Λ_m = 516 ohm^{-1} $cm.^2$ $mole^{-1}$ at 25° for the tri-divalent salt $Y_2(SO_4)_3$; and Λ_m = 768 ohm^{-1} $cm.^2$ $mole^{-1}$ at 25° for $Cr_2(SO_4)_3$.

The values of the magnetic moments μ_{eff} (Table II) show that the bipyO_2–metal complex cations have the same number of unpaired electrons as the "free" metal ions. The tris-chelate cations of the elements from Mn(II) to Zn(II) therefore may be considered to have an octahedral structure utilizing $4s4p^34d^2$ hybrid orbitals, similar to other transition metal complexes of oxygen donor ligands.[13] The Mn(III) complex ion, $[Mn(bipyO_2)_3]^{3+}$, recently reported by Nyholm and Turco, also was found to be of the spin-free type.[17]

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Infrared Studies of 2,2′-Bipyridine N,N′-Dioxide and its Metal Complexes in the 3–38 μ Region

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The infrared spectra of 2,2′-bipyridine N,N′-dioxide (bipyO_2) and of eighteen of its metal complexes were measured in the range 4000–260 $cm.^{-1}$. The band appearing in the cesium bromide region of the spectra of the complexes but not in that of free bipyO_2 was assigned to the metal-to-oxygen stretching vibration. The trend of the frequency values of this band for the various metal complexes is similar to that observed for the complexes of pyridine N-oxide, and is in qualitative agreement with the Irving and Williams stability series. In the spectra of the complexes the bands corresponding, respectively, to the metal-to-oxygen and oxygen-to-nitrogen stretching vibrations were found to be correlated.

In the preceding paper[1] the preparation and properties of 2,2′-bipyridine N,N′-dioxide (bipyO_2) and of a number of its metal complexes were described. The present paper deals with the infrared spectra of bipyO_2 and of eighteen of its metal complexes (Table I), and assignments are made for the most significant absorption bands. In most cases these assignments are based on a comparative study of the spectra of bipyO_2 and of related molecules such as pyridine,[2] pyridine N-oxide,[3–6] and biphenyl.[7] Reference is also made to the theoretical[8] and experimental work[9] on *o*-disubstituted benzene type molecules.

The infrared spectrum of bipyO_2 resembles that of pyridine N-oxide (pyO) and the assignments made in the former are based largely on our study of the latter.[4,5] The frequency shifts and the intensity variations observed when comparing the spectra of bipyO_2 metal complexes with the spectrum of the free bipyO_2 also are similar to those reported for pyO metal complexes and free pyO.[4,5]

Experimental

The infrared spectra were obtained as described previously.[10] Figures 1 and 2 show two typical spectra in the sodium chloride (1700–650 $cm.^{-1}$) and in the cesium bromide (650–260 $cm.^{-1}$) regions. Table I lists the compounds investigated, together with the values of the NO stretching, NO bending, and MO stretching frequencies.

Preparation of $[Cu(bipyO_2)_2][PtCl_4]\cdot 4D_2O$.—Finely powdered anhydrous $[Cu(bipyO_2)_2][PtCl_4]$ was introduced in a vacuum desiccator together with D_2O, and the system was immediately

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