and $TlNO_3 \cdot 4TU$ belong to the same group of structures within the family, despite the differences in stoichiometry. In $TlClO_4 \cdot 4TU$ the space available to both cations and anions is fully occupied; in $Pb(NO_3)_2 \cdot 6TU$ the space available to the anions is fully occupied but there are now only half as many cations per anion and so only two-thirds of the cation positions are occupied (the absence of random occupancy of these sites indicates that chemical factors also play a role); in $TlNO_3 \cdot 4TU$ the cation sites are fully occupied and it is the requirement of electrical neutrality which prevents more anions from entering the structure even though there is space available for their accommodation. On the other hand the $Pb(ClO_4)_2 \cdot 6TU$ complex is appreciably different; the first type of structural arrangement (like that in $Pb(NO_3)_2 \cdot 6TU$) is not possible because the perchlorate ions are too large to allow insertion in the interchain channels of the additional anions needed to compensate for the extra positive charge of Pb^{2+} compared to M^+. Thus a considerable change of structure is required and this occurs by omission of alternate cation–thiourea chains, the anion arrangements being similar in $TlClO_4 \cdot 4TU$ and $Pb(ClO_4)_2 \cdot 6TU$. From these results we infer that, given the general structure type, the detailed crystal structures depend mainly on anion size and shape.

Notes

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Preparation of $Co(dipy)_2X_2^+$ Complexes ($X^- = Cl^-, Br^-, I^-, NO_2^-$) by Controlled Oxidative Processes

BY A. A. VLČEK[1]

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In the series $Co(dipy)_2X_2^+$ only substances with $X^- = Cl^-$,[2] NO_2^-,[3,4] acetate,[5] and $Co(dipy)_2CO_3^+$,[2] as well as $Co(dipy)_3^{3+}$,[2,6] have been described. In most preparations of these complexes the main step consists of the oxidation of divalent cobalt complexes with hydrogen peroxide or oxygen. However, this method is not suitable for preparation of other complexes (*e.g.*, for $X^- = I^-$), and the reaction with oxygen or hydrogen peroxide as oxidation agents is not a straightforward operation.

A recent study of complexes of the general type $Co(dipy)_2X_2$[7] has shown that these complexes undergo, in most cases, a very easy oxidation and that they can be used as starting material for the preparation of the corresponding series of trivalent cobalt complexes. In case an oxidation agent is used, the reduced form of which enters the coordination sphere, the desired complex is formed in one step without any formation of intermediates.

Results and Discussion

Bis-Halogeno Complexes.—The previous studies on $[Co(dipy)_2Cl_2]Cl$[2-4a] have shown that this complex undergoes extremely rapid hydrolysis in aqueous solution. However, the solutions in alcohol are much more stable than the aqueous solutions.

The general method for the preparation of bis-halogeno complexes of the type $[Co(dipy)_2X_2]^+$ makes use of the fact that the solubility of the corresponding divalent complex in methanol is rather high and that the divalent complex undergoes an immediate and clean oxidation with the corresponding halogen. The resulting trivalent complex, being much less soluble than the starting material, separates from solution. In this way the previously known $[Co(dipy)_2Cl_2]Cl$, as well as the new complexes $[Co(dipy)_2I_2]I$ and $[Co(dipy)_2Br_2]Br$, has been prepared.

The chloro complex results in the form of a mixture of *cis* and *trans* isomers which can be separated by fractional crystallization from boiling ethanol. Upon reaction with water, both forms dissolve to give red-violet solutions and spectrophotometric studies show the presence of the bis-aquo form in solution (see Table I). Both isomers dissolve in methanol and ethanol without decomposition.

$[Co(dipy)_2I_2]I$ and $[Co(dipy)_2Br_2]Br$ complexes precipitate in the form of dark violet and brownish green crystalline powders, respectively. They are slightly soluble in methanol and ethanol and almost insoluble in water. The solubility in alcohols can be enhanced by adding lithium or sodium perchlorate or lithium chloride.

When a mixture of $CoCl_2$ and dipyridyl in the ratio 1:3 or 1:4 is oxidized with the halogen (in the presence of the corresponding lithium halogenide) the bis-halogeno species is formed (in yields of 30–40%) together with tris-dipyridyl complex.

The polarographic behavior of the system cobalt(II)–dipyridyl shows that there exists a rather rapid equilibrium between various cobalt(II)–dipyridyl com-

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(1) On leave of absence from the J. Heyrovský Institute of Polarography, Czechoslovak Academy of Sciences, Prague, Czechoslovakia; recipient of a Senior Foreign Scientist National Science Foundation fellowship, 1964–1965.

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TABLE I

SPECTRAL PROPERTIES OF SOME $[Co(dipy)_2X_2]^+$ COMPLEXES

I^- [a]		Br^- [a]		Cl^- [a,b]		H_2O [c]		NO_2^-		CO_3^{2-}		
ν [d]	ϵ [e]	ν	ϵ	ν	ϵ	ν	ϵ	ν	ϵ	ν	ϵ	
15,980	125	16,650	130	17,100	100	19,700	70	22,700	300	19,850	110	Lf bands
				18,300	125							
23,300 sh [f]	4,000	23,600	1700			27,000 sh	4000	29,000	10,000	26,300 sh	...	Charge-transfer bands
28,000	13,000											
32,300 sh	...	31,000 sh				32,300	33,000	31,300 sh	...	32,800	30,000	Dipyridyl bands
33,400	51,000	32,100	38,000			33,300	33,000	32,500	37,000			
34,000		33,200	40,000			34,500 sh	...			38,800	37,000	
40,000 sh	...	39,000 sh	...			38,500	36,000	41,000	30,000	40,200	37,000	
51,000	60,000	51,000	52,000			49,000	47,000	51,000	50,000	51,000	45,000	

[a] In methanol. [b] Solution spectra were identical for *cis* and *trans* isomers. [c] Prepared in solution only by dissolving *cis*- or *trans*-$[Co(dipy)_2Cl_2]Cl$ in water or by the acidification of the solution of $[Co(dipy)_2CO_3]NO_3$. [d] Units: cm^{-1}. [e] Units: $M^{-1}\,cm^{-1}$. [f] sh denotes shoulder on the main band.

plexes.[7] On the basis of this fact the formation of tris-dipyridyl species could be expected even for ratios Co:dipy less than 1:3. The fact that there is no appreciable amount of the tris-dipyridyl species formed at ratios 1:2 and only about 50% at the ratio 1:3 points to the conclusion that the oxidative attack is fastest for the bis-dipyridyl complex (any rapid exchange of dipyridyl ligands in the oxidized form is highly improbable).

Bis-Nitro Complex.—The original preparation of $[Co(dipy)_2(NO_2)_2]Cl$[3,4a] was based on the substitution of chloride ions in the $[Co(dipy)_2Cl_2]^+$ by nitrite ions.

A one-step preparation uses the fact that the complex of divalent cobalt $[Co(dipy)_2(NO_2)_2]$[7] undergoes a very easy oxidation. The oxidation by air leads to rather complicated products. On the other hand, acidification of an aqueous solution of $CoCl_2$ and dipyridyl in the ratio 1:2 which contains a slight excess of sodium nitrite results in immediate oxidation and formation of the $[Co(dipy)_2(NO_2)_2]^+$ salt in the crystalline form. However, as the course of the preparation and the polarographic study show, the process proceeds through several intermediates, the nature of which is being studied.

The complex cation $[Co(dipy)_2(NO_2)_2]^+$, unlike the corresponding bis-halogeno cations, is rather stable in aqueous solutions and undergoes only a very slow hydrolysis in aqueous solutions.

The chloride dissolves quite easily in water and methanol. The perchlorate, on the other hand, is much less soluble.

Attempts to separate the expected *cis* and *trans* isomers by fractional crystallization or precipitation from aqueous or ethanolic solutions were unsuccessful.

The infrared bands attributable to NO_2^- groups are located at 1420 (s), 1305 (s), 827 (m), and 819 cm^{-1} (m). The position of the last two bands is identical with that of the corresponding bands of $Co(en)_2(NO_2)_2^+$, which are at 820 and 827 cm^{-1}, respectively. There is no band attributable to the group NO_2^- in the region 900–1200 cm^{-1}, showing that the complex prepared contains metal–nitrogen bonds and has to be regarded as the bis-nitro complex.

Spectral Properties of $[Co(dipy)_2X_2]^+$ Complexes.—Table I summarizes the ultraviolet and visible spectra of the newly prepared complexes together with the spectral properties of some analogous complexes. All complexes show three types of bands: ligand field bands of low intensity, bands of medium intensity, which are probably due to the intramolecular charge-transfer processes, and very strong bands due to internal dipyridyl transition. This assignment is made on the basis of the intensity of the bands, the positions of the band maxima, and the influence of the composition of the complex on the position and intensity of the bands. These can be easily seen in Table I. It is interesting to note that the internal dipyridyl bands depend to a great extent upon the composition of the coordination sphere, as can be seen also by comparison with dipyridyl complexes of other transition metals.[8]

The low-intensity ligand field bands show the normal sequence of the spectrochemical series, *i.e.*, $I^- < Br^- < Cl^- < H_2O < CO_3^{2-} <$ dipy $< NO_2^-$. The position of NO_2^- ligand in this series confirms the previous conclusion that the complex contains a metal–nitrogen bond.

Experimental Section

Preparation of $[Co(dipy)_2(NO_2)_2]Cl\cdot 2H_2O$.—$CoCl_2\cdot 6H_2O$ (2 g) was dissolved in 70 ml of water, the solution was deaerated, and 2.6 g of dipyridyl was added under strong stirring. After dissolution of dipyridyl, solid sodium nitrite was added in a nitrogen atmosphere until the precipitate started to form. Then 2 ml of concentrated hydrochloric acid was added. The solution was cooled with ice and 15 ml of concentrated hydrochloric acid was added. The resulting mixture was stirred and bubbled with nitrogen. After about 30 min the crystals were filtered off, washed with 1:1 hydrochloric acid, and redissolved in a small volume of lukewarm water. The solution, originally reddish brown, turned yellow, and yellow crystals were formed after a few minutes. The solution was cooled with ice; the crystals were filtered off and washed with small amounts of cooled hydrochloric acid and with ethanol and ether. *Anal.* Calcd for $[Co(dipy)_2NO_2)_2]Cl\cdot 2H_2O$: C, 44.9; N, 15.73; H, 3.76; Cl, 6.70. Found: C, 44.96; N, 15.07; H, 4.00, Cl, 6.92.

Preparation of $[Co(dipy)_2(NO_2)_2]ClO_4$.—This salt can be prepared from the chloride by precipitation with sodium perchlorate or by the analogous procedure as for chloride using concentrated perchloric acid instead of HCl (1 and 8 ml, respectively). *Anal.* Calcd for $[Co(dipy)_2(NO_2)_2]ClO_4$: C, 42.68; N, 14.94; H, 2.85. Found: C, 43.0; N, 14.42; H, 3.3.

Preparation of $[Co(dipy)_2I_2]I$.—$CoCl_2\cdot 6H_2O$ (1 g) was dissolved

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in 50 ml of methanol and 1.3 g of dipyridyl and 1 g of sodium iodide were added under nitrogen. To the resulting solution a solution of 0.55 g of iodine in 20 ml of ethanol was slowly added with mixing. Dark violet crystals were formed which after filtering off were washed several times with small volumes of methanol. *Anal.* Calcd for $[Co(dipy)_2I_2]I$: C, 31.92; N, 7.45; H, 2.16, I, 50.5. Found: C, 31.05; N, 7.24; H, 2.75; I, 51.0.

Preparation of $[Co(dipy)_2Br_2]Br$.—The procedure was the same as for the iodide, an equivalent amount of sodium bromide and bromine being used. *Anal.* Calcd for $[Co(dipy)_2Br_2]Br$: C, 39.60; N, 9.17; H, 2.64; Br, 39.15. Found: C, 39.45; N, 8.95; H, 3.05, Br, 41.5.

Preparation of $[Co(dipy)_2Cl_2]Cl$.—One gram of $CoCl_2 \cdot 6H_2O$, 1 g of lithium chloride, and 1.6 g of dipyridyl were successively dissolved in 50 ml of dry methanol under nitrogen. Gaseous chlorine was then slowly introduced into this solution under cooling for 15 min. The resulting crystals were filtered off and washed with methanol. They were redissolved in ethanol on a water bath and the ethanol was slowly evaporated on the boiling water bath. After a while green needles of the *trans* isomer started to form on the walls of vessel. The hot solution was decanted and the remaining crystals were washed several times with cold ethanol and ether and dried. Further slow evaporation of the solution at room temperature resulted in the formation of violet crystals of the *cis* isomer which were filtered off and washed with ethanol and ether. *Anal.* Calcd for $[Co(dipy)_2Cl_2]Cl \cdot 3H_2O$: C, 45.6, N, 10.53; H, 4.14; Cl, 20.02. Found: C, 45.08; N, 10.40; H, 4.05; Cl, 20.17.

Spectra.—A Cary Model 14 spectrophotometer was used. Infrared spectra were taken on a Perkin-Elmer Model 337 grating infrared spectrophotometer in Nujol mulls.

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Spin Delocalization in γ-Picoline N-Oxide Coordinated with Bis(1,1,1-trifluoro-2,4-pentanedionato)copper(II)[1]

By Rudolph W. Kluiber and William DeW. Horrocks, Jr.

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Proton magnetic resonance evidence for electron spin delocalization in the π orbitals of heterocyclic N-oxides[2,3] and in σ orbitals of heterocyclic amines axially coordinated to nickel(II) and cobalt(II) 2,4-pentanedionates[3,4] has been recently reported. Copper(II) β-diketonates are also known to coordinate with various ligands such as heterocyclic bases to give pentacoordinate[5] and hexacoordinate[6] species in which the added ligands are presumed to be axially disposed. In the present work nmr isotropic shifts of the protons in γ-picoline N-oxide complexed with bis(1,1,1-trifluoro-2,4-pentanedionato)copper(II) $[Cu(CF_3COCHCOCH_3)_2$, herein referred to as $Cu(TFAA)_2]$, were obtained and compared with the previous results.

Experimental Section

Bis(1,1,1-trifluoro-2,4-pentanedionato)(γ-picoline N-oxide)-copper(II).—A mixture of 0.37 g (0.001 mole) of $Cu(TFAA)_2$ and 0.11 g (0.001 mole) of γ-picoline N-oxide was dissolved in 14 ml of hot toluene. Heptane (15 ml) was added and the solution allowed to cool slowly. The turquoise-green crystals which separated, 0.40 g, were recrystallized twice from toluene–heptane. After drying *in vacuo* at 55° the product melted 149.5–150°.

Anal. Calcd for $C_{16}H_{15}F_6NO_5Cu$: C, 40.13; H, 3.16; N, 2.93. Found: C, 40.28; H, 3.22; N, 2.69.

Magnetic Moments.—These were obtained by the Gouy method for solids and by the method of Evans[7] for solutions. A diamagnetic correction of 202×10^{-6} cgs unit was made for the 1:1 complex.

Optical Spectra and Equilibrium Constants.—Optical spectra were obtained using a Cary Model 14 recording spectrophotometer. Equilibrium constants were evaluated at about 23° using as solvent chloroform purified immediately before use by washing with concentrated sulfuric acid, water, bicarbonate solution, and water, drying, and distilling. At 14,300 cm^{-1} the molar extinction (ϵ) of $Cu(TFAA)_2$ is 32 l. $mole^{-1}$ cm^{-1}, and that of the complex was taken to be 54 l. $mole^{-1}$ cm^{-1} by extrapolation. For γ-picoline N-oxide $\epsilon \sim 0$ at this frequency.

Electron Spin Resonance.—The spectrum of a powdered sample was obtained using a Varian instrument operating at a frequency of 35 kMcps. The *g* values were obtained directly from the spectrum without recourse to computer construction. A solution spectrum was obtained using a spectrometer frequency of approximately 10 kMcps.

Nuclear Magnetic Resonance.—The proton spectra were obtained in deuteriochloroform, purified by standing over sodium bicarbonate and anhydrous magnesium sulfate and distilling just prior to use with tetramethylsilane as an internal standard. Experimental results were duplicated using $Cu(TFFA)_2$ and independently using a recrystallized sample of the 1:1 γ-picoline N-oxide:$Cu(TFAA)_2$ complex. All solids were dried just prior to use. Some irreversible decomposition of the complex occurred at higher temperatures so variable temperature runs were carried out starting at the lowest temperature using a freshly prepared solution. In all cases the general temperature dependence given in Figure 1 could be repeated, although some broadening of the line widths and downfield shifts of the resonances was always noted after heating the samples even as low as 60°.

Mass Spectrometry.—A fragmentation pattern of the 1:1 $Cu(TFAA)_2$:γ-picoline N-oxide was obtained using an A.E.I. MS 9 spectrometer. The observed copper-bearing fragments, identified by their characteristic copper 63:65 ratio, were in the order of decreasing abundance: $Cu(TFAA)_2$, $Cu(TFAA)_2$–CF_3, $Cu(TFAA)_2$–CH_3CO, a fragment of molecular weight 231, and Cu(TFAA). In all cases the cleavage fragments were also observed.

Bis(1,1,1-trifluoro-2,4-pentanedionato)(γ-picoline N-oxide)zinc(II).—To the hydrate of $Zn(TFAA)_2$ in toluene was added a stoichiometric amount of γ-picoline N-oxide. The water was removed azeotropically. A white crystalline precipitate, mp 135.5–136.5°, was recovered by filtration after standing overnight. The nmr spectrum at 39° showed peaks at 497 (α), 435 (β), 146 (γ-CH_3), 125 (CH_3), and 348 (CH) cps from TMS.

Anal. Calcd for $C_{16}H_{15}F_6NO_5Zn$: C, 39.99; H, 3.14; N, 2.91. Found: C, 40.30; H, 3.42; N, 3.02.

Results

$Cu(TFAA)_2$ interacts with N-oxides to form addition complexes of 1:1 and under some conditions 2:1 stoichiometry. The 1:1 γ-picoline N-oxide:$Cu(TFAA)_2$ complex in its crystalline form has a magnetic moment of 1.94 BM. Its powder esr spectrum was re-

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