The selection rules can be confirmed qualitatively by a group-theory consideration of the wave functions, ψ_n and ψ_m, over the entire chain. For the d_{xz}, d_{yz} bands, ψ_n is e_g if n is odd and e_u if n is even. For the d^*_{xy} band, ψ_m is b_{2g} if m is odd and b_{1u} if m is even. The product e_ub_{2g} or e_gb_{1u} gives e_u which is the representation for the dipole vector normal to the chain. Hence such transitions are allowed between odd and even states. For the other bands, although transitions u ↔ g are possible, none of the appropriate products yields the required a_{2u} or e_u representations for the dipole vector.

The quantity $H_{j,j+1}$ for d_{xy} orbitals should be negative, corresponding to bonding; hence the state $n = 1$ is the totally bonding or lowest energy MO in the band. However, $H_{j,j+1}$ for d_{xz} and d_{yz} orbitals are positive and the state $n = 1$ is totally antibonding or the highest in energy. The transitions between the bands will therefore be broadened by the sum of the widths of the two bands. The fact that the observed dipole-allowed absorption peak is quite narrow is additional evidence for only weak overlap of d orbitals and corresponding interactions between adjacent atoms. Thus the $(\mathbf{r})_{j,j+1}$, which measures the extent of $\pi \rightarrow \Delta$ charge transfer between two adjacent platinum atoms, is much smaller than the charge-transfer moments between the ligands and the platinum.

The experimental observation of a single dipole-allowed but weak transition polarized normal to the chains is therefore very nicely explained by the band theory involving the interactions between the d orbitals on adjacent metal atoms. Enhancement of the absorption in the direction of the chains (*c*) is apparently a consequence of the same factors which influence the corresponding intensities in MGS. To this end it would be interesting to determine if there has been a shift to lower frequencies of a high-intensity band in the crystal and whether this band is highly polarized in the *c* direction as in the case of MGS. Continuing studies are in progress with the objective of improving the quality of the spectra.

Contribution from the Department of Chemistry,
Worcester Polytechnic Institute,
Worcester, Massachusetts 01609

Reformulation of Previously Reported *trans*-Dichlorobis(1,10-phenanthroline)cobalt(III) Complexes

By L. H. Berka and R. R. Gagne

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The preparation of the *trans*-$Co(NN)_2Cl_2^+$ cation, where NN = 1,10-phenanthroline or 2,2′-bipyridine, has been reported by several workers.[1–4] Recently, it was shown[5] that one such complex,[3] *trans*-$[Co(bipy)_2Cl_2]Cl$, is actually a mixture of *cis*-$Co(bipy)_2Cl_2^+$ and $Co(bipy)_3^{3+}$ cations and $CoCl_4^{2-}$ and Cl^- anions. While investigating various techniques to assign *cis*–*trans* configurations to complexes of this type, we have been led to reinvestigate the corresponding phen complexes.

Experimental Section

Apparatus and Analyses.—Visible spectra were measured with Cary 14 and Beckman DK2-A spectrophotometers. X-Ray powder patterns were obtained using Ni-filtered X-radiation from a copper source and a Philips Debye–Scherrer type powder camera. Conductivities were measured at 25° using a Yellow Springs Instrument bridge, Model 31. Elemental analyses were performed by Baron Consulting Co., Orange, Conn., and Alfred Bernhardt, Mülheim (Ruhr), Germany.

$[\mathrm{Co(phen)_3}][\mathrm{CoCl_4}]_3\cdot 2\mathrm{HCl}$.—The green compound reported as *trans*-$[Co(phen)_2Cl_2]Cl\cdot 2HCl$ in ref 1 was synthesized exactly according to the reported instructions and repeated several times with similar results. *Anal.* Calcd for $C_{72}H_{50}Cl_{14}Co_5N_{12}$: C, 46.14; H, 2.69; N, 8.97; Cl, 26.48. Found: C, 46.44; H, 2.94; N, 9.15; Cl, 27.06. An aqueous solution (10^{-3} *M*) of the dried (−2HCl) material gave a molar conductance of 1675 ohm^{-1} (calcd,[6] 1650 ohm^{-1}).

$[Co(phen)_3](ClO_4)_3\cdot 3H_2O$ was prepared as a derivative of the green compound by passing a solution (0.4 g in 20 ml of concentrated HCl) of the material through an anion-exchange resin (Cl^- form). The resulting yellow solution was diluted to 50 ml and excess sodium perchlorate was added until precipitation was complete. The yellow product was isolated and washed twice with ethanol. *Anal.* Calcd for $C_{36}H_{30}Cl_3CoN_6O_{15}$: C, 45.42; H, 3.18; N, 8.83; Cl, 11.17. Found: C, 45.79; H, 2.93; N, 8.90; Cl, 11.76.

$[(C_4H_9)_4N]_2CoCl_4$ was prepared as a second derivative by slow addition of tetrabutylammonium chloride to a solution of the green material (0.5 g in 20 ml of concentrated HCl). When precipitation seemed complete, the blue product was isolated, washed with ethanol and ether, and dried in air over $CaCl_2$. *Anal.* Calcd for $C_{32}H_{72}Cl_4CoN_2$: C, 56.05; H, 10.58; N, 4.09; Cl, 20.68. Found: C, 56.54; H, 10.30; N, 4.27; Cl, 20.61.

Aqueous solutions of the compound had a dirty yellow color, consistent with the simultaneous presence of yellow $Co(phen)_3^{3+}$ and pink $Co(H_2O)_6^{2+}$. Stable green HCl solutions gave visible spectra characteristic of the $CoCl_4^{2-}$ species (575–750 mμ).

cis-**$[\mathrm{Co(phen)_2Cl_2}][\mathrm{Co(phen)_3}][\mathrm{CoCl_4}]_2\cdot 3\mathrm{H_2O}$.**—The green compound reported as *trans*-$[Co(phen)_2Cl_2]^+(H_7O_3)^+Cl^-{}_2$ in ref 2 was synthesized several times with similar results. *Anal.* Calcd for $C_{60}H_{46}Cl_{10}Co_4N_{10}O_3$: C, 46.63; H, 3.00; N, 9.06; Cl, 22.94; Co, 15.25. Found: C, 46.73; H, 3.06; N, 9.03; Cl, 23.63, 23.16; Co, 15.17, 15.06. An aqueous solution (10^{-3} *M*) of the material gave a molar conductance of 1060 ohm^{-1} (calcd,[6] 1050 ohm^{-1}).

A voluminous mixed precipitate of *cis*-$[Co(phen)_2Cl_2]ClO_4\cdot 3H_2O$ and $[Co(phen)_3](ClO_4)_3\cdot 3H_2O$ resulted on addition of excess $NaClO_4$ to a concentrated aqueous solution of the compound. Surprisingly, these two compounds separated into two distinct layers on centrifugation. Repeated washings with water of the violet layer yielded a product having a powder pattern identical with that of the known *cis* compound.[7]

Visible spectra of the stable green HCl solutions of the material showed peaks characteristic of $CoCl_4^{2-}$. When these solutions were passed through cation-exchange resins (H^+ form),

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(1) P. Pfeiffer and B. Werdelmann, *Z. Anorg. Chem.*, **262**, 31 (1950).

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(6) Assuming (a) hydrolysis of $CoCl_4^{2-}$ in aqueous solution to give Co^{2+}(aq), (b) molar conductances of 450, 250, and 100 ohm^{-1} for $[Co(phen)_3]Cl_3$, $CoCl_2$, and *cis*-$[Co(phen)_2Cl_2]Cl$, respectively, and (c) additivity of these molar conductances.

(7) A. V. Ablov, *Russ. J. Inorg. Chem.*, **6**, 157 (1961).

bright blue solutions resulted, while passage through anion resins gave dirty yellow solutions. Aqueous solutions of the material had a dirty yellow color, consistent with the simultaneous presence of yellow $Co(phen)_3{}^{3+}$, violet *cis*-$Co(phen)_2Cl_2{}^+$, and pink $Co(H_2O)_6{}^{2+}$.

Vlcek's Product.—Attempts were made to produce the green compound reported as *trans*-$[Co(bipy)_2Cl_2]Cl \cdot 3H_2O$ in ref 4. Very minute quantities of a green material were isolated but in insufficient quantity for further investigation. Most attempts yielded only the violet *cis* isomer.

Results

The green compound reported as *trans*-$[Co(phen)_2Cl_2]Cl \cdot 2HCl$ by Pfeiffer and Werdelmann[1] is reformulated as $[Co(phen)_3]_2[CoCl_4]_3 \cdot 2HCl$. The green compound reported as *trans*-$[Co(phen)_2Cl_2]^+(H_7O_3)^+Cl^-_2$ by Miller and Prince[2] is reformulated as *cis*-$[Co(phen)_2Cl_2][Co(phen)_3][CoCl_4]_2 \cdot 3H_2O$. These new formulations are consistent with evidence presented in the Experimental Section.

Discussion

After completion of this work, Gibson and coworkers[8] reported the preparation of the Pfeiffer and Werdelmann product but gave results differing significantly from ours. Mixtures were obtained when the Pfeiffer and Werdelmann procedure was followed, with *cis*-$[Co(phen)_2Cl_2][CoCl_3(H_2O)][H_{2n}O_n]Cl \cdot (2.5 - n)H_2O$ being a common formulation. Contrary to these results, our product has been shown to contain the *tris* cation by isolation of the corresponding perchlorate derivative (no derivatives were isolated in the Gibson work). In addition there are large differences in the observed C, H, and N values. The product reported as $[Co(phen)_3][phenH][CoCl_4]_2 \cdot HCl$ in ref 8, which most closely resembles our formulation, was not obtained by the exact Pfeiffer and Werdelmann method. Other reaction products given in ref 8 were also obtained by variations in the procedure, and, hence, comparison of these products to our formulation is not valid.

Both *trans*-$[Co(py)_4Cl_2]Cl$ and *trans*-$[Co(en)_2Cl_2]Cl$ are green and previous workers have assigned the *trans* configuration to analogous bipy and phen complexes on this basis. In the two cases reported here the green color results from the simultaneous presence of yellow $Co(phen)_3{}^{3+}$ and blue $CoCl_4{}^{2-}$.

It appears from our results and those of others[5,8] that, even though several compounds appear in the literature as containing *trans*-$Co(NN)_2Cl_2{}^+$ cations of phen and bipy, there is at present no independently substantiated example of such a cation. Rund has shown[9] that phen ligands in such *trans* species experience mutual repulsions by the protons at the 2 and 9 positions and this represents an unfavorable energetic situation in the case of Rh. In the Co case one would expect this repulsion to be even more severe. Hence, if such *trans* cations of Co are ever isolated, it is probable that they will have geometries severely distorted from a regular *trans* arrangement.

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Contribution from the Chemistry Department,
University of Hawaii, Honolulu, Hawaii 96822

The Reaction between Phosphorus Trichloride and 1,1-Dimethylhydrazine

By Daisy B. Whigan, John W. Gilje, and Amy E. Goya[1]

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In 1961 Holmes[2] reported that PCl_3 reacts with excess H_2NCH_3 to form $P_4(NCH_3)_6$. He assigned this compound a cage structure in which the four phosphorus atoms occupy the corners of a tetrahedron with the NCH_3 groups bridging the edges. As part of an extensive study of the reactions between $R_{3-n}PCl_n$ and methylhydrazines Nielson and Sisler[3] investigated the corresponding reaction between excess $H_2NN(CH_3)_2$ and PCl_3. On the basis of the ratio of phosphorus trichloride used to the hydrazine hydrochloride produced they assumed the reaction to be

$$PCl_3 + 6H_2NN(CH_3)_2 \longrightarrow P\{HNN(CH_3)_2\}_3 + 3H_2NN(CH_3)_2 \cdot HCl \quad (1)$$

An uncharacterized product was postulated to be the trihydrazide, $P\{NHN(CH_3)_2\}_3$. However, if a reaction analogous to the phosphorus trichloride–methylamine reaction is written for the 1,1-dimethylhydrazine case

$$4PCl_3 + 18H_2NN(CH_3)_2 \longrightarrow P_4\{NN(CH_3)_2\}_6 + 12H_2NN(CH_3)_2 \cdot HCl \quad (2)$$

the $PCl_3 : H_2NN(CH_3)_2 \cdot HCl$ ratio of 1:3 is identical with the corresponding ratio for reaction 1. As a similarity in reactivity with PCl_3 between methylhydrazines and corresponding primary amines has previously been noted[4] we decided to reinvestigate the reaction between PCl_3 and $H_2NN(CH_3)_2$ to determine if the trihydrazide was actually produced.

Experimental Section

All manipulations were performed in a vacuum line or under a dry nitrogen atmosphere using standard techniques.[5] Phosphorus trichloride (Matheson Coleman and Bell) and 1,1-dimethylhydrazine (Aldrich Chemical Co.) were distilled immediately before use. All other solvents and reactants were dried and/or purified by appropriate means.

All nmr spectra were recorded in H_2CCl_2 solutions in a Varian A-60 spectrometer at about 35°. Chemical shifts were observed relative to the H_2CCl_2 singlet. The δ values reported in this paper have been converted to a tetramethylsilane reference by

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