ties as high as 0.1–1 M H^+. The variation of the first-order rate constant, k, with hydrogen ion concentration is expressed fairly well by eq 3. At 70° the acid-dependent term, k_2, contributes less than 10% to the first-order rate constant at $[H^+] = 1.0\ M$. It is likely that the acid-dependent term corresponds to a path involving *trans*-$Cr(NH_3)_4(OH)Cl^+$ as the active species. We have observed that the base hydrolysis reactions of both *cis*- and *trans*-$Cr(NH_3)_4(OH_2)Cl^{2+}$ are complete within a few minutes at room temperature, these reactions being the basis of the preparations of the diaquotetraammine complexes. A direct study of the aquation kinetics of *cis*- and *trans*-$Cr(NH_3)_4(OH)Cl^+$ is in progress and will be the subject of a separate report.

$$k = k_1 + \frac{k_2}{[H^+]} \qquad (3)$$

The trends in the relative rates of the reactions of Table I are the same as Garner and coworkers[2-4] have reported for the analogous ethylenediamine complexes. The change from Cl to Br as the leaving ligand increases the rate of aquation, the dihalo complexes aquate much more rapidly than the haloaquo complexes, and the *cis* isomer of $Cr(NH_3)_4(OH_2)Cl^{2+}$ aquates more rapidly than does the *trans* isomer. Specifically, Br^- is lost at least 8.7 times as rapidly as Cl^- from *trans*-$Cr(NH_3)_4BrCl^+$, and the loss of Br^- from the bromochloro ion is about 10 times as rapid as the loss of Cl^- from *trans*-$Cr(NH_3)_4Cl_2^+$, when the aquation rate constant for the latter complex is corrected for the statistical factor. The difference in aquation rates between *cis*- and *trans*-$Cr(NH_3)_4(OH_2)Cl^{2+}$ is smaller than reported[4] for the analogous ethylenediamine complexes. This smaller effect of geometry may be due to the ability of the nitrogen ligands of the ammonia complexes to move independently of each other, whereas the two nitrogen atoms of ethylenediamine molecule must act in concert. As was noted earlier, the reactions studied here occur with essentially complete retention of configuration, which is again similar to the behavior of the analogous ethylenediamine complexes.

Since the data of Table I show that *cis*-$Cr(NH_3)_4(OH_2)Cl^{2+}$ aquates more rapidly than *trans*-$Cr(NH_3)_4(OH_2)Cl^{2+}$, a possible reaction mechanism for the aquation of the *trans*-chloroaquo ion would seem to be isomerization to the *cis*-chloroquo ion, followed by aquation. This proposal may be rejected on the basis of reaction stoichiometry. The *cis* isomer aquates to give *ca.* 100% *cis*-$Cr(NH_3)_4(OH_2)_2^{3+}$, whereas the *trans* isomer yields largely the *trans*-$Cr(NH_3)_4(OH_2)_2^{3+}$ ion.

Arrhenius activation energies, calculated from the data of Table I, are 24 ± 1 kcal mol^{-1} for *trans*-$Cr(NH_3)_4(OH_2)Cl^{2+}$, 22.0 ± 0.5 kcal mol^{-1} for *cis*-$Cr(NH_3)_4(OH_2)Cl^{2+}$, 21.6 ± 0.3 kcal mol^{-1} for *trans*-$Cr(NH_3)_4Cl_2^+$, and 20.8 ± 0.3 kcal mol^{-1} for *trans*-$Cr(NH_3)_4BrCl^+$. The activation energy for *trans*-$Cr(NH_3)_4(OH_2)Cl^{2+}$ was calculated from the data for $[H^+] = 1.0\ M$.

Acknowledgments.—The authors are grateful to the National Science Foundation for financial support of this work.

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Physicochemical and Spectral Properties of Octahedral Dioxomolybdenum(VI) Complexes

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Received June 3, 1968

Complexes of the type MoO_2L_2 (where L = acetylacetonate, benzoylacetonate, $(C_6H_5CO)_2CH^-$, oxinate, $(CH_2)_4NCS_2^-$, and $R_2NCS_2^-$, where R = CH_3, C_2H_5, n-C_3H_7, or n-C_4H_9) were examined to determine whether they contained *cis*-MoO_2 groups. The infrared spectra of these complexes all show two strong Mo=O stretching modes in the 900-cm^{-1} region as expected for a *cis*-MoO_2 group. These complexes were found to be undissociated by conductivity measurements in CH_3NO_2 and $HCON(CH_3)_2$. The large values of the dipole moments of $MoO_2[(C_2H_5)_2NCS_2]_2$ (9.51 D), $MoO_2[(n\text{-}C_3H_7)_2NCS_2]_2$ (8.05 D), and $MoO_2[(n\text{-}C_4H_9)_2NCS_2]_2$ (7.60 D) confirm the presence of bent MoO_2 groups in these complexes. The presence of *cis*-MoO_2 groups for $MoO_2(C_5H_7O_2)_2$ and $MoO_2[(C_6H_5CO)_2CH]_2$ was indicated by their nmr spectra. It was concluded that all octahedral dioxomolybdenum(VI) complexes prepared to date contain *cis*-MoO_2 groups. The electronic spectra of the β-diketonates possess a charge-transfer band due to the molybdenyl group near 52,000 cm^{-1}, and a similar band occurs in the dithiocarbamate complexes above 53,000 cm^{-1}. The molybdenum(V) complex, $[(C_5H_7O_2)_2Mo{=}O]_2O$, also possesses a charge-transfer band assignable to a $O \rightarrow Mo(V)$ transition above 53,000 cm^{-1}. Peaks assignable to charge transfer from the ligand donor atoms to molybdenum(VI) were located in the 26,000–31,000 cm^{-1} region.

Introduction

In a previous study[1] of dioxomolybdenum(VI) dialkyldithiocarbamate complexes, $MoO_2(R_2NCS_2)_2$, it was concluded from infrared spectral evidence that these complexes and analogous complexes contain *cis* (bent) dioxomolybdenum groups. The presence of a *cis*-MoO_2 group in $MoO_2[(CH_3)_2NCS_2]_2$ was recently pro-

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[1] F. W. Moore and M. L. Larson, *Inorg. Chem.*, **6**, 998 (1967).

posed by Cotton and Wing[2] on the basis of the appearance of two strong $Mo{=}O$ stretching modes in the 900-cm^{-1} region of its infrared spectrum. Nonlinear MoO_2 groups were also suggested for the related $MoO_2X_4^{2-}$ anions, where $X = F$ or Cl, from infrared spectral evidence[3-5] and this proposal was confirmed by the X-ray structure determination of $K_2MoO_2F_4$.[6] In the absence of any X-ray structural data for dioxomolybdenum(VI) complexes with bidentate ligands, it was decided to confirm the presence of a *cis*-MoO_2 group in these complexes by other methods, such as nmr spectroscopy and dipole moment studies, which are more reliable than infrared data alone. In addition, the ultraviolet spectra of these materials were examined to study the nature of the charge-transfer bands of the dioxomolybdenum(VI) group.

Experimental Section

The 1-pyrrolidinecarbodithioic acid (sodium salt) was obtained from the J. T. Baker Chemical Co. and the dimethyldithiocarbamic acid (sodium salt) was obtained from the Aldrich Chemical Co. The secondary amines and β-diketones were obtained from Eastman Organic Chemicals and were used without further purification. The solvents used for the conductivity and spectral measurements were Matheson Coleman and Bell Spectroquality. The remaining materials were reagent grade chemicals, used without further purification.

All melting points were obtained in sealed capillaries and were corrected. Molybdenum contents were determined by ignition to MoO_3 at 525° and the organic microanalyses were performed by Huffman Laboratories, Inc., Wheatridge, Colo.

The infrared spectra (4000–400 cm^{-1}) were recorded using a Perkin-Elmer Corp. Model 21 instrument and the visible–ultraviolet spectra (14,000–53,000 cm^{-1}) were obtained using a Beckman Model DK-2A instrument. Conductance measurements were made at 25.00 ± 0.05° and 3000 cps using an Industrial Instruments Model RC-18 instrument with a Freas-type solution cell having bright platinum electrodes and a cell constant of 0.409 cm^{-1}. The dielectric constants were measured at 25.0 ± 0.05° with a Kahl Scientific DM-01 Dipolmeter. Densities were determined at 25 ± 0.01° using a Weld specific gravity bottle. The proton nmr spectra were determined on a Varian Associates HA-100 spectrometer or on a Varian A-60 spectrometer using tetramethylsilane as internal standard.

The molybdenum(VI) dialkyldithiocarbamate and molybdenum(V) alkylxanthate complexes were prepared as previously described[1] and purified by repeated crystallization. The molybdenyl(VI) bisacetylacetonate was prepared by the method of Jones[7] and purified by crystallization from acetylacetone–petroleum ether (bp 30–60°). The molybdenum(V) acetylacetonate complex, $[(C_5H_7O_2)_2Mo{=}O]_2O$, was prepared by the aerial oxidation of $Mo(C_5H_7O_2)_3$[8] and purified by repeated recrystallization from acetylacetone. The molybdenyl(VI) complex of 8-quinolinol (oxine), $MoO_2(C_9H_6NO)_2$, was prepared by the procedure of Vogel[9] and was found to have a melting point of 356–361° dec.

$MoO_2[(CH_2)_4NCS_2]_2$.—Dioxomolybdenum(VI) bis(1-pyrrolidinecarbodithioate) was prepared by the dropwise acidification at 5° of a solution of $Na_2MoO_4 \cdot 2H_2O$ (4.84 g, 0.0200 mol) and $(CH_2)_4NCS_2Na$ (5.85 g, 0.0346 mol) in 300 ml of water with 30 ml of 1.5 *N* HNO_3. After the solution was stirred for 15 min, the copious precipitate was filtered and washed with water. The dried solid (4.02 g, 55.3% yield) was recrystallized from CH_2Cl_2–petroleum ether (bp 30–60°) to obtain a fine, orange-yellow solid. It decomposed without melting at 175–180°. *Anal.* Calcd for $MoO_2[(CH_2)_4NCS_2]_2$: C, 28.57; H, 3.84; N, 6.66; S, 30.51; Mo, 22.82. Found: C, 28.56; H, 3.93; N, 6.78; S, 30.74; Mo, 24.04. The following peaks were observed in the 1700–650-cm^{-1} region: 1515, 1504 (vs, doublet), 1477 (s), 1451 (vs), 1337 (s), 1253 (w), 1220 (w), 1183 (m), 1160 (s), 1000 (vs), 943 (vs), 913 (s), 866 (s), 830 (m), 719 (w).

$MoO_2[(C_6H_5CO)_2CH]_2$.—Dioxomolybdenum(VI) bis(1,3-diphenyl-1,3-propanedionate) was prepared by the briefly described procedure of Morgan and Castell.[10] A stirred suspension of MoO_3 (2.00 g, 0.0139 mol) and dibenzoylmethane (6.23 g, 0.0278 mol) was heated to 200° over a 2-hr period. The cooled tar was washed with ether by decantation, stirred with 30 ml of $CHCl_3$, and filtered. The addition of petroleum ether (bp 30–60°) to the filtrate yielded a light brown, crystalline solid (1.41 g, 18.4% yield). Recrystallization from benzene–petroleum ether yielded a yellow solid, mp 194–196° dec, lit.[10] mp 112°). *Anal.* Calcd for $MoO_2(C_{30}H_{22}O_4)$: C, 62.73; H, 3.86; Mo, 16.70. Found: C, 63.06; H, 4.03; Mo, 16.14.

Because the melting point of this product was much higher than that previously reported, the compound was prepared by modifying the method of Stevens[11] for the preparation of the oxine complex. A solution of dibenzoylmethane (4.60 g, 0.0205 mol) in 80 ml of absolute ethanol was added to a stirred solution of $Na_2MoO_4 \cdot 2H_2O$ (2.49 g, 0.0103 mol) in 50 ml of water and 15 ml of 2 *N* HCl. The yellow precipitate, which formed immediately, was filtered and washed with water. It was recrystallized rapidly from benzene–petroleum ether (bp 30–60°) and yielded 1.49 g (25.2% yield) of bright yellow, finely crystalline solid, mp 197–198° dec. The recrystallization must be completed rapidly since benzene solutions undergo decomposition in about 15 min. *Anal.* Calcd for $MoC_{30}H_{22}O_6$: Mo, 16.70. Found: Mo, 16.10. The following peaks were found for this material as a Nujol mull in the 1700–650-cm^{-1} region: 1605 (s), 1560 (s), 1553 (s), 1520 (vs), 1310 (m), 1294 (m), 1227 (m), 1186 (w), 1124 (w), 1064 (m), 1025 (m), 1002 (w), 931 (s), 899 (s), 817 (w), 787 (w), 758 (s, br), 704 (s), 676 (s). The ligand absorption bands are similar to those of other metal–dibenzoylmethane complexes.[12] It must be concluded that the melting point given in the literature[10] is incorrect even though the product reported had the correct stoichiometry on analysis.

$MoO_2[CH_3COCHCOC_6H_5]_2$.—The method of Morgan and Castell[10] was used to prepare dioxomolybdenum(VI) bis(1-phenyl-1,3-butanedionate); prior attempts using modifications of the Jones[7] and Stevens procedures[11] were unsuccessful. A stirred suspension of MoO_3 (4.45 g, 0.0309 mol) and 1-phenyl-1,3-butanedione (10.00 g, 0.0617 mol) was heated for 12 hr at 105° in an open flask. The reaction mixture was stirred with 40 ml of ether and filtered. The insoluble portion was stirred with 40 ml of CH_2Cl_2 and filtered to obtain a greenish filtrate that was vacuum evaporated. The light green residue was recrystallized from CH_2Cl_2–petroleum ether (bp 30–60°) to yield 0.84 g (6.0% yield) of yellow, crystalline solid (mp 181–182° dec, lit.[10] mp 98°). *Anal.* Calcd for $MoC_{20}H_{18}O_6$: C, 53.37; H, 4.03; Mo, 21.31. Found: C, 52.58; H, 4.10; Mo, 21.53. The infrared spectrum as a KBr disk of this material in the 1700–650-cm^{-1} region showed the following peaks: 1613 (s), 1577 (s), 1527 (s), 1502 (s), 1462 (m), 1431 (m), 1374 (s), 1321 (m), 1294 (s), 1217 (m), 1188 (m), 1111 (m), 1075 (w), 1034 (m), 1005 (w), 966 (m), 941 (s), 909 (s), 855 (m), 820 (w), 794 (m), 781 (m), 709 (m, br), 685 (s, br). This infrared spectrum is comparable to that of other metal 1-phenyl-1,3-butanedionates.[12]

Attempts to prepare dioxomolybdenum(VI) β-diketonate complexes either by acidification techniques or by the heating of β-

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diketones with MoO_3[10] using 3,5-heptanedione, 1,1,1-trifluoro-2,4-pentanedione, or 1,1,1,5,5,5-hexafluoro-2,4-pentanedione were unsuccessful.

Results and Discussion

Conductance Measurements.—Conductance measurements were made on dilute solutions (0.1–1.0 mM) of these complexes in N,N-dimethylformamide (DMF), CH_3NO_2, or CH_3CN to determine whether the complexes were undissociated. The values obtained were in the range of 0.1–1.0 ohm^{-1} cm^2 mol^{-1} which are much lower than the values of 70–160 ohm^{-1} cm^2 mol^{-1} obtained for 1:1 electrolytes in these solvents.[13,14] Thus it can be concluded that these complexes are undissociated and six-coordinate.

Infrared Spectra.—The infrared spectra of the dioxomolybdenum complexes show two Mo=O stretching modes in the 900-cm^{-1} region as expected for a bent MoO_2 group[2,5] (Table I). These bands appear at higher energy in solution, as compared with the solid-state spectra, implying that intermolecular attraction has been lessened. The values of the force constant (k) and the interaction constant (k_i) were calculated using the secular equations of Cotton and Wing[2] for C_{2v} symmetry for the MoO_2 group. The solution data were used for these calculations since the assumption of an undistorted O=M=O angle of 90° should be valid for dilute solutions. For $MoO_2(C_5H_7O_2)_2$, the k and k_i values agree with the values for the other complexes if the band at 948 cm^{-1} is assigned to the symmetric Mo=O mode rather than if both bands are assumed to be degenerate at 909 cm^{-1}. A definite assignment had not been previously made because acetylacetonates show medium to strong absorption at about 930 cm^{-1}. The use of solutions did not separate this band at 948-cm^{-1} into a ligand band and an Mo=O band; however, from the intensity of this band and by comparison with the other β-diketone complexes, it appears that the symmetric Mo=O stretching mode occurs at 948 cm^{-1}.

When the force constant correlations of Cotton and Wing[2] are used, these complexes would be expected to have an Mo—O bond order of about 2.4 and an Mo—O bond distance of about 1.7 Å. An analogous compound $K_2MoO_2F_4$, which has strong Mo=O stretching modes at 940 and 905 cm^{-1}, was found to have an O–Mo–O angle of 95° and Mo—O distances of 1.69 and 1.73 Å by a recent X-ray determination.[6] These results show that the force constant correlations can be used with some reliability and the original correlations have been extended by Grandjean and Weiss using further X-ray and infrared data.[15] The bending mode of the MoO_2 group was not examined since it would be expected to appear below 400 cm^{-1}, as in other compounds.[5] Infrared data[1] and Raman data[4,5] indicate that all octahedral dioxomolybdenum(VI) complexes studied to date contain a bent MoO_2 group. Infrared studies show that complexes of tungsten dioxodihalides probably also contain a bent WO_2 group.[16,17]

TABLE I

INFRARED SPECTRA OF THE MoO_2^{2+} GROUP[a]

Compound	Media	Sym Mo=O, cm^{-1}	Anti-sym M=O, cm^{-1}	Force constant,[b] dyn/Å	Interaction constant,[b] dyn/Å
$MoO_2(C_5H_7O_2)_2$	Nujol	935	904		
	DMF	948	909[c]	7.30	0.63
	$CHBr_3$	948	907		
$MoO_2(CH_3COCHCOC_6H_5)_2$	KBr	939	909		
	DMF	941	911	7.20	0.50
$MoO_2[(C_6H_5CO)_2CH]_2$	Nujol	931	899		
	C_6H_6	946	914	7.26	0.51
	DMF	937	909		
$MoO_2(oxinate)_2$	Nujol	924	898		
	DMF	932	914	7.04	0.29
$MoO_2[(CH_3)_2NCS_2]_2$	Nujol	912	876		
	$CHBr_3$	915	881	6.80	0.53
$MoO_2[(C_2H_5)_2NCS_2]_2$	Nujol	905	877		
	$CHBr_3$	916	877		
	DMF	913	880	6.77	0.51
$MoO_2[(n\text{-}C_3H_7)_2NCS_2]_2$	Nujol	909	875		
	C_6H_6	915	882	6.76	0.48
	DMF	913	880		
$MoO_2[(n\text{-}C_4H_9)_2NCS_2]_2$	Nujol	909	877		
	C_6H_6	917	882	6.83	0.54
	DMF	913	879		
$MoO_2[(CH_2)_4NCS_2]_2$	Nujol	943	913	7.22	0.49

[a] The assignments used are those of Cotton and Wing.[2] [b] Calculations based on a normal 90° O–Mo–O angle for C_{2v} symmetry. [c] If the 909-cm^{-1} band is assumed to be degenerate, then the force constant is 6.67 dyn/Å and interaction constant is −0.005 dyn/Å.

Dipole Moment Measurements.—The dipole moment calculations were made according to the method of Halverstadt and Kumler[18,19] and the data were treated by the least-squares method. The values of the electronic polarization of the solutes were estimated by using the ligand values of Malatesta[20] and of Gur'yanova and Kuzina,[21] and, following Malatesta, 10 ml was used for the molybdenum atom and 2 ml for the molybdenyl oxygen. No corrections were made for atomic polarization since they would be insignificant. The dipole moment data obtained are summarized in Table II. No measurements could be obtained for the molybdenyl β-diketonates because of their insolubility or instability in appropriate solvents. Since other symmetrical metal dithiocarbamates have low dipole moments[20,21] and a complex with a *trans*-MoO_2 group would be expected to have a small dipole moment, it can be concluded that these complexes contain a bent MoO_2 group in agreement with the infrared data. These values are also in good agreement with those obtained by Kraus and Huber[22] for $MoO_2Cl_2 \cdot (CH_2CO)_2O$ (6.85 D) and for $MoO_2Cl_2[CH_2(CO_2C_2H_5)_2]$ (8.26 D) where a bent MoO_2 group is also postulated.

Nuclear Magnetic Resonance.—The proton nmr spectra of the molybdenyl β-diketonates were determined in $CDCl_3$ (Table III). The nmr spectrum of

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TABLE II

DIPOLE MOMENT DATA

Compound	P_2, ml[a]	P_e, ml[b]	P_o, ml[c]	μ, D[d]
$MoO_2[(C_2H_5)_2NCS_2]_2$	1954.5	108	1847	9.51
$MoO_2[(n\text{-}C_3H_7)_2NCS_2]_2$	1445.7	122	1324	8.05
$MoO_2[(n\text{-}C_4H_9)_2NCS_2]_2$	1323.7	130	1194	7.60

[a] Total polarization. [b] Electronic polarization. [c] Orientation polarization. [d] Dipole moment; calculated using the formula $\mu = 0.01281\sqrt{P_oT}$.

$MoO_2(C_5H_7O_2)_2$ was compared with that of $SnCl_2(C_5H_7O_2)_2$ since this material is known to have a *cis* configuration.[23] It can be concluded that $MoO_2(C_5H_7O_2)_2$ contains a bent MoO_2 group since its nmr spectrum possess a single 3-H peak and the CH_3 groups give rise to two peaks of equal intensity. The interpretation of the spectrum of the benzoylacetonate is complicated by the fact that the ligand is unsymmetrical and it is possible to have a bent MoO_2 group without the CH_3 or C_6H_5 peaks being split.[24] For the molybdenyl complex, the nmr spectrum does not differentiate between *cis*- or *trans*-MoO_2 groups since no evidence was found for the isomer designated "*cis,cis,cis*" by Serpone and Fay,[24] which would have split CH_3 and C_6H_5 peaks. The C_6H_5 spectrum of the dibenzoylmethane derivative consists of a series of several lines and is more complicated than the C_6H_5 spectrum of benzoylacetonate complex. Because of its complexity, it appears that C_6H_5 peaks are probably split, which is in agreement with the fact that this complex must contain a bent MoO_2 group. The nmr spectra of $MoO_2[(C_2H_5)_2NCS_2]_2$, $MoO_2[(n\text{-}C_3H_7)_2NCS_2]_2$, and $MoO_2[(n\text{-}C_4H_9)_2NCS_2]_2$ in $CDCl_3$ show only *n*-alkyl patterns since the alkyl groups are presumably too far removed from the coordination sphere to be affected. It can be concluded that the nmr data and dipole moment measurements confirm the infrared evidence that these complexes contain bent MoO_2 groups.

TABLE III

NUCLEAR MAGNETIC RESONANCE MEASUREMENTS IN $CDCl_3$[a]

Compound	Proton chemical shifts, $-\delta$, ppm		
	CH_3	$=\overset{\overset{H}{\vert}}{C}-$	C_6H_5[c]
$MoO_2(C_5H_7O_2)_2$	2.12, 2.14	5.88	. . .
$SnCl_2(C_5H_7O_2)_2$[b]	2.11, 2.20	5.69	. . .
$MoO_2(CH_3COCHCOC_6H_5)_2$	2.23	6.37	7.37, 7.75
$MoO_2(C_6H_5COCHCOC_6H_5)_2$	. . .	6.99	7.28, 7.83

[a] Tetramethylsilane = 0.00. [b] Reference 23. [c] Centers of multiplets.

Visible–Ultraviolet Spectra.—From a study of some MoO_2^{2+} complexes, Bartecki[25,26] concluded that bands in the 27,000–30,000-cm^{-1} region may be assigned to a transition from the molybdenyl oxygen to an empty molybdenum orbital and that bands in this region are characteristic of the molybdenyl group. The spectra of the dioxomolybdenum(VI) complexes and some related Mo(V) complexes were examined in an attempt to confirm the presence of this absorption (Table IV). From assignments given for other oxinates,[27] the bands of the MoO_2^{2+} complex at 27,250 and 31,650 cm^{-1} can be assigned to ligand N→Mo and ligand O→Mo transitions, respectively, and this complex apparently possesses strong N–Mo bonding.

TABLE IV

VISIBLE–ULTRAVIOLET SPECTRA

Compound	Media	Absorption bands,[a] 10^3 cm^{-1}
$MoO_2(\text{oxinate})_2$	CH_2Cl_2	27.3 (4.00), 31.7 sh (3.72), 40.0 (4.70)
$MoO_2(C_5H_7O_2)_2$	CH_2Cl_2	31.5 (3.73), 38.2 (4.09)
	CH_3CN	31.6 (3.80), 38.4 (3.97), 48.8 (4.04), 52.1 (4.16)
$Mo_2O_3(C_5H_7O_2)_4$	CH_3CN	20.6 (4.03), 25.0 (4.03), 30.6 (4.19), 40.0 (4.30), >53.0
$MoO_2(CH_3COCHCOC_6H_5)_2$	CH_3CN	29.0 (4.24), 36.6 (4.47), 48.2 (4.68)
$MoO_2[(C_6H_5CO)_2CH]_2$	CH_3CN	26.3 (4.42), 35.3 (4.48), 41.5 (3.90), 50.0 (4.52), 52.1 (4.69)
$MoO_2[(CH_3)_2NCS_2]_2$	CH_3CN	26.5 (3.46), 33.3 (3.88), 39.5 (4.40), 48.8 (4.65), >53.0
$MoO_2[(C_2H_5)_2NCS_2]_2$	C_6H_6	26.9 (3.58), 33.7 sh (3.88)
	CH_3CN	26.5 (3.48), 33.3 sh (4.04), 39.3 (4.44), 48.5 (4.42), >53.0
$MoO_2[(n\text{-}C_3H_7)_2NCS_2]_2$	CH_3CN	26.5 (3.55), 33.3 (4.07), 39.2 (4.44), 46.1 sh (4.24), 48.8 (4.28), >53.0
$MoO_2[(n\text{-}C_4H_9)_2NCS_2]_2$	CH_3CN	26.3 (3.58), 33.3 (4.10), 39.2 (4.47), 45.5 sh (4.27), 48.8 (4.36), >53.0
$Mo_2O_3(C_2H_5COCS_2)_4$	CH_3CN	19.8 (3.98), 32.3 sh (3.94), 37.6 (4.38), 45.3 (4.54), 50.0 (4.45)

[a] sh = shoulder; log ϵ values are given in parentheses.

The band found in the 26,000–31,000-cm^{-1} region in the spectra of metal β-diketonates is usually assigned to ligand π–π^* charge transfer,[28,29] but it is also possible for this band to contain some ligand O→metal pπ–dπ character.[30] Although a definite transition due to the MoO_2 group has not been found near 30,000 cm^{-1} for these β-diketonates, an intense band assignable to molybdenyl O→Mo charge transfer has been located near 52,000 cm^{-1}. This assignment is reasonable since MoO_4^{2-} and $MoO_2S_2^{2-}$ show[31] a comparable band at 47,000 cm^{-1}. The molybdenum(V) acetylacetonate complex shows the beginning of an intense peak at 53,000 cm^{-1} which is probably due to charge transfer from the doubly bonded oxygen to Mo(V).

The spectra of the dithiocarbamate complexes, in addition to the S→Mo charge-transfer bands[1] near 26,000 cm^{-1} and ligand bands,[32] show the beginning of an intense band at 53,000 cm^{-1} assignable to the MoO_2 group. The molybdenum(V) xanthate complex shows no band below 53,000 cm^{-1} that can be assigned to O→Mo(V) charge transfer since the peak near 50,000 cm^{-1} also occurs in the potassium salt.

It is not now possible to say whether a definite molyb-

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denyl band occurs near 30,000 cm^{-1}; if present, these bands may be obscured in the currently investigated complexes by the ligand to molybdenum charge-transfer bands. Evidence has been found for a molybdenyl oxygen to molybdenum transition around 52,000 cm^{-1}, which would be expected by analogy to molybdate anion. More work with simple compounds, preferably by reflectance spectroscopy, will be necessary to confirm the existence of a molybdenyl band near 30,000 cm^{-1}.

Acknowledgment.—The authors are grateful to Dr. R. C. Taylor and Dr. F. Parker, Department of Chemistry, University of Michigan, for determining the nmr spectra.

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Formation and Dissociation Kinetics of Bis(2,4,6-tripyridyl-*s*-triazine)iron(II)

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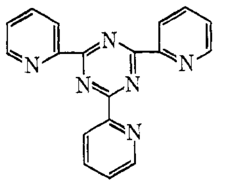
Received August 20, 1968

The kinetics of formation of bis(2,4,6-tripyridyl-*s*-triazine)iron(II), $Fe(TPTZ)_2^{2+}$, fit a mechanism where the addition of the first TPTZ is rate determining and the addition of the second TPTZ is much faster. The rate of dissociation of $Fe(TPTZ)_2^{2+}$ is determined using acid, EDTA, or base to cause the reaction. With high concentrations of these scavengers present to react either with Fe(II) or with TPTZ, the rate-determining step shifts to the removal of one TPTZ from $Fe(TPTZ)_2^{2+}$. One of the TPTZ ligands must dissociate completely before EDTA can react; however, EDTA does react with the mono-TPTZ complex. On the other hand, hydrogen ion (above 10^{-3} *M*) and hydroxide ion (above 10^{-10} *M*) react directly with the bis complex to accelerate the dissociation. The $Fe(TPTZ)^{2+}$ complex also shows a strong kinetic preference to react with a neutral TPTZ molecule rather than with the negatively charged EDTA ion.

Introduction

The ligand 2,4,6-tripyridyl-*s*-triazine, TPTZ, first prepared by Case and Koft,[3] forms a 2:1 iron(II) complex with a molar absorptivity equal to 21,600 at 593 mμ. The complex has been used for iron determinations.[4-6] Only the bis complex has been observed and 1:1 mixtures disproportionate to the bis complex and free iron.[7-9]


TPTZ

Kratochvil and White observed a rapid reaction between EDTA and $Fe(TPTZ)_2^{2+}$ and used the reaction to determine trace levels of EDTA.[10] One of the reasons we examined this reaction was to see if a direct attack of EDTA on the bis-TPTZ complex occurred since such direct attack is not observed in the much slower reaction with tris(1,10-phenanthroline)iron(II).[11,12] Another reason was to compare the mechanism of dissociation in acid and in base to that of tris(1,10-phenanthroline)iron(II).[11,13-16]

This study shows that EDTA does not react directly with the bis complex although the reaction rates are quite fast requiring stopped-flow techniques. The dissociation kinetics are fascinatingly complex with regard to pH dependence. An additional complication results because of a strong kinetic preference of $Fe(TPTZ)^{2+}$ to react with another TPTZ returning to reactants rather than to react with the electrostatically more attractive EDTA anion to give products.

Experimental Section

The TPTZ (G. F. Smith Chemical Co.) was dissolved with the aid of a few drops of concentrated HCl to give a 3.04×10^{-3} *M* solution. Iron(II) solutions were prepared from fresh ferrous ammonium sulfate. The $Fe(TPTZ)_2^{2+}$ complex was prepared ($\sim 10^{-4}$ *M*) using a slight excess of TPTZ to ensure complete complexation of the metal. Spectrophotometric standardization at 593 mμ was used. EDTA solutions were prepared from the recrystallized sodium salt and standardized against copper.

Constant ionic strength was maintained at 0.10 *M* with KCl. Sodium acetate–acetic acid buffer (0.02 *M*) was used from pH 3.5 to 5.5. At higher and lower pH EDTA served as its own

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