$Ph_2PHMo(CO)_5$, 18399-61-6; $Ph_2PMeMo(CO)_5$, 18497-62-6; $Ph_2PEtMo(CO)_5$, 18497-63-7; (c-Hx)$PH_2Mo(CO)_5$, 72868-89-4; (c-Hx)$_2PHMo(CO)_5$, 72868-90-7; $AsMe_3Mo(CO)_5$, 72868-91-8; $AsBu_3Mo(CO)_5$, 72868-92-9; $AsPh_3Mo(CO)_5$, 19212-22-7; $SbBu_3Mo(CO)_5$, 72868-93-0; $SbPh_3Mo(CO)_5$, 19212-21-6; (η^6-C_6H_6)$Cr(CO)_2P(OMe)_3$, 31852-04-7; (η^6-C_6H_6)$Cr(CO)_2P(OEt)_3$, 53611-65-7; (η^6-C_6H_6)$Cr(CO)_2P(OCH_2CH_2Cl)_3$, 72868-94-1; (η^6-C_6H_6)$Cr(CO)_2P(O$-*i*-Pr$)_3$, 72868-95-2; (η^6-C_6H_6)$Cr(CO)_2P(OPh)_3$, 72868-96-3; (η^6-C_6H_6)$Cr(CO)_2PBu_3$, 12278-02-3; (η^6-C_6H_6)$Cr(CO)_2P$(c-Hx)$_3$, 12278-74-9; (η^6-C_6H_6)$Cr(CO)_2PPh_3$, 12278-67-0; (η^6-C_6H_6)$Cr(CO)_2PhPH_2$, 72868-97-4; (η^6-C_6H_6)$Cr(CO)_2PhP$(c-Hx)$_2$, 72868-98-5; (η^6-C_6H_6)$Cr(CO)_2Ph_2PH$, 72868-99-6; (η^6-C_6H_6)$Cr(CO)_2Ph_2PEt$, 72869-00-2; (η^6-C_6H_6)$Cr(CO)_2Ph_2P$(c-Hx), 72869-01-3; (η^6-C_6H_6)$Cr(CO)_2$(c-Hx)PH_2, 72869-02-4; (η^6-C_6H_6)$Cr(CO)_2$(c-Hx)$_2$PH, 72869-03-5; $Ph_2P(CH_2)_2AsPh_2Ni(CO)_3$ (As bonded), 72869-04-6.

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Infrared Metal–Ligand Vibrations of Hexaaquametal(III) Ions in Alums

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Received November 2, 1979

The infrared spectra of mulls of the cesium β-alums $CsM^{III}(SO_4)_2\cdot12H_2O$ (M^{III} = Al, Ti, V, Cr, Fe) and of the ammonium and potassium α-alums of Al^{III} and Cr^{III} are reported between 300 and 1200 cm^{-1} at ambient temperature, together with that of the α-alum $CsCo(SO_4)_2\cdot12H_2O$ between 450 and 1200 cm^{-1} at about 80 K. Only two bands are observed to shift appreciably with change in the trivalent metal ion; these are assigned to the antisymmetric metal–ligand stretch ν_3 and the antisymmetric metal–ligand bend ν_4 of the $M(H_2O)_6^{3+}$ complex. These assignments are confirmed by the observation of metal isotope shifts of 5 and 1 cm^{-1}, respectively, between cesium chromium alums enriched in ^{50}Cr and ^{53}Cr.

Introduction

There have been remarkably few vibrational studies of the $M(H_2O)_6^{3+}$ species[1–7] and assignments of the M^{III}–OH_2 stretching frequencies remain elusive. Most reports are on individual compounds, and, although some assignments have been aided by deuteration, few comparative studies have been reported. The alums, of composition $M^I(H_2O)_6M^{III}(H_2O)_6(XO_4)_2$, provide a series of compounds in which the trivalent metal ion can be systematically varied, usually in isomorphous structures. This advantage is somewhat offset, however, by the presence of the $M(H_2O)_6^+$ species, which contributes additional vibrations due to the coordination sphere of the monovalent cation.

This study reports the infrared mull spectra of the cesium sulfate alums of Al, Ti, V, Cr, Fe, and Co. Comparison of these spectra allows a clear assignment of the two infrared active M^{III}–OH_2 vibrations. The cesium alums were chosen because it is possible to obtain stable specimens containing the $Co(H_2O)_6^{3+}$ species[8] and because crystal structure determinations of all of the compounds are available.[9–11] This series does not contain the Sc alum, and we were unable to obtain reliable spectra of the Mn alum, which decomposed under the conditions used in recording the other spectra.

Experimental Section

The cesium alums were prepared from reagent grade chemicals either by using methods described in the literature (Al,[9] V,[8] Cr,[8] Fe[8]) or by the procedures described below. They were recrystallized from 1 M H_2SO_4 unless stated otherwise and characterized by their infrared spectra, by single-crystal X-ray structure determinations, and in some cases by their melting points. The ammonium and potassium alums were recrystallized commerical samples. The isotope-enriched chromium alums were prepared by oxidizing enriched chromium(III) oxide obtained from Oak Ridge National Laboratory with perchloric acid to chromium(VI) oxide and then proceeding as above.

The cesium titanium alum was prepared under an inert atmosphere. Cesium sulfate (1 g) was dissolved in 30 mL of deoxygenated 1 M sulfuric acid. Addition of 7 mL of a deoxygenated 15% w/v solution of titanium trichloride gave a violet solution. Storage under refrigeration gave violet crystals which were collected, washed with 1 M sulfuric acid, and recrystallized from 1 M sulfuric acid. The crystals are unstable in air and were stored under a nitrogen atmosphere.

The cesium manganese alum[12] was prepared by adding with stirring a solution of 3.6 g of cesium sulfate in 5 mL of 30% sulfuric acid to a solution of 5.3 g of freshly prepared manganese(III) acetate[13] in 30 mL of 30% sulfuric acid cooled to 0 °C. The mixture was kept at 3 °C for 3 days while crystallization occurred. The product is very susceptible to decomposition by heat and by dehydration but can be kept in the mother liquor at low temperatures.

The cesium cobalt alum[8] was prepared by electrolysis of cobalt(II) sulfate for 5 h at 0.2 A, producing a large deposit of blue microcrystals. Aging these under refrigeration for 1 week produced larger crystals which were collected by filtration and washed with 17 M acetic acid followed by dry ether.

Infrared spectra were recorded on a Perkin-Elmer Model 580 spectrometer, generally using cesium iodide plates. With the manganese and cobalt alums, oxidation of the iodide in the plates occurs.

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(1) Campbell, J. A.; Ryan, D. P.; Simpson, L. M. *Spectrochim. Acta, Part A* **1970**, *26a*, 2351.

(2) Petrov, K. I.; Bol'shakova, N. K.; Kravchenko, V. V.; Iskhakova, L. D. *Russ. J. Inorg. Chem.* (*Engl. Transl.*) **1970**, *15*, 1529.

(3) Strupler, N.; Guillermet, J.; Hoffelt, J.; Froment, F. *Bull. Soc. Chim. Fr.* **1974**, 1830.

(4) Eysel, H. H.; Eckert, J. *Z. Anorg. Allg. Chem.* **1976**, *424*, 68.

(5) Eckert, J.; Eysel, H. H.; Kampfmeyer, G. L. *Z. Anorg. Allg. Chem.* **1976**, *424*, 81.

(6) Adams, D. M.; Hills, D. J. *J. Chem. Soc., Dalton Trans.* **1978**, 782. Note that the labels ρ_t and ρ_w should be interchanged in the table on p 787.

(7) James, D. W.; Whitnall, J. M. *J. Raman Spectrosc.* **1978**, *7*, 225.

(8) Johnson, D. A.; Sharpe, A. G. *J. Chem. Soc. A* **1966**, 798.

(9) Cromer, D. T.; Kay, M. I.; Larsen, A. C. *Acta Crystallogr.* **1966**, *21*, 383.

(10) Sygusch, J. *Acta Crystallogr., Sect. B* **1974**, *30*, 662.

(11) Best, S. P.; Beattie, J. K.; Skelton, B. W.; White, A. H., to be submitted for publication.

(12) Christensen, O. T. *Z. Anorg. Chem.* **1901**, *27*, 329.

(13) Brauer, G. "Handbook of Preparative Inorganic Chemistry", 2nd ed.; Academic Press: New York, 1963.

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Table I. Infrared Absorption Band Maxima (cm^{-1}) for Nujol Mulls of Alums $M^IM^{III}(SO_4)_2 \cdot 12H_2O$

M^IM^{III}	$\nu_3(SO_4)$	$\rho_w(H_2O^{III})$	$\rho_r(H_2O^{III})$	$\nu_4(SO_4)$	$\nu_3(M^{III}O_6)$	$\rho_w(H_2O^I)$	see text	$\nu_4(M^{III}O_6)$
CsAl	1093	934	673	610	588	489	445	355, 335
CsCo[a]	1086	920	680	610	570	523	445	
CsCr	1089	932	667	609	555	485	444	329
CsV	1089	930	668	607	532	483	445	320
CsTi	1090	932	670	607	520	484	445	308
CsFe	1086	933	668	607	505	480	445	304
KAl[b]	1190 1093 1063	921	690	609	592	550	468	345
NH_4Al[b]	1188 1093 1070	918	690	609	592	528		
KCr[b]	1185 1085 1058	911	685	612	556	500	460	325
NH_4Cr[b]	1165 1082 1035	917	688	609	554	515	460	324

[a] At about 80 K. [b] $\nu_1(SO_4)$ observed at 970, 972, 973, and 976 cm^{-1} for KAl, NH_4Al, KCr, and NH_4Cr alums, respectively.

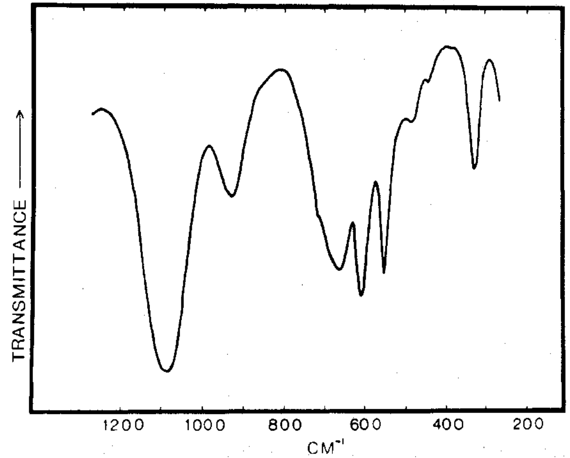

Figure 1. Infrared mull spectrum of $CsCr(SO_4)_2 \cdot 12H_2O$.

Sodium chloride plates were used for spectra above 700 cm^{-1}, and for lower frequencies a thin film of polyethylene was used to protect the cesium iodide plates. A liquid-nitrogen-cooled sample holder with KBr windows was used to reduce decomposition in the heat of the beam. This enabled the spectra to be recorded down to 450 cm^{-1} for the cobalt alum, but reliable spectra of the manganese alum were not obtained.

Hence, the infrared mull spectra of the cesium alums of Al, Ti, V, Cr, and Fe were recorded between 4000 and 250 cm^{-1} at room temperature and that of the Co alum between 4000 and 450 cm^{-1} at close to liquid-nitrogen temperature. Hexachloro-1,3-butadiene was used as the mulling agent for the spectra above 2000 cm^{-1} and Nujol for the spectra below 2000 cm^{-1}. Preliminary experiments using KBr disks indicated that the mulling agents masked none of the absorption bands. Mulls were prepared by addition of the mulling oil to the sample before grinding, in order to eliminate problems of dehydration.

Results and Discussion

In this report attention is focused on the spectrum between 1200 and 300 cm^{-1}. The internal water vibrations—HOH bending and OH stretching modes—occur at higher frequencies. These are closely related to the hydrogen bonded structures of the alums and will be reported separately. Below 1200 cm^{-1} are the vibrations of the sulfate ion, the external vibrations of the coordinated water molecules, and the vibrations of the MO_6 octahedra. The frequencies observed are listed in Table I, and a typical spectrum is illustrated in Figure 1.

Sulfate Vibrations. The vibrational modes of the sulfate ion are readily identified by one or more of the following means: (i) comparison with known frequencies observed in simple sulfate salts, (ii) comparison with the selenate alums, and (iii) their frequency invariance with changes in the metal ions of the alums. For the sulfate ion in tetrahedral symmetry only the two antisymmetric modes ν_3 (stretching) and ν_4 (bending) are infrared active, but, in the lower symmetry of the crystal, factor group analysis[4] predicts infrared activity of ν_1, two ν_2, three ν_3, and three ν_4 modes. Of these the three ν_3 stretching modes occur as a broad degenerate band at 1090 ± 4 cm^{-1} in each of the cesium alums. In the sulfate ion this frequency is observed[14] at 1105 cm^{-1}, and in the selenate $CsAl(SeO_4)_2 \cdot 12H_2O$ it is absent.[2] In two previous studies of $CsAl(SO_4)_2 \cdot 12H_2O$ the maximum of this broad band has been reported at 1110[2] and at 1103[3] cm^{-1}. In contrast with the single broad ν_3 band observed in the cesium alums, the three ν_3 components predicted by factor group analysis are observed in the ammonium and potassium alums of both aluminum and chromium (Table I). In each case the strongest mode occurs at about 1090 cm^{-1}, with weaker bands on either side between 1035 and 1190 cm^{-1}.

The absence of these additional ν_3 bands in the cesium alums is a reliable indication of the integrity of the sample, for they appear if the sample has partly decomposed through, for example, dehydration.

The identification of the ν_4 bending mode at 607–610 cm^{-1} is similarly straightforward. The previous studies of $CsAl(SO_4)_2 \cdot 12H_2O$ reported this frequency at 614[2] and at 615[3] cm^{-1}, and it occurs at 611 cm^{-1} in the sulfate ion.[14]

The ν_1 sulfate stretching frequency is totally symmetric in tetrahedral symmetry and occurs at 986 and 987 cm^{-1} in different orientations in the Raman spectrum[4] of $CsAl(SO_4)_2 \cdot 12H_2O$. It is expected to be weak in intensity in the infrared spectrum of the cesium alums which, on the evidence of the single observed ν_3 band, do not distort the sulfate ion much from tetrahedral symmetry. A strong band observed[3] at 970 cm^{-1} in the spectrum of $CsAl(SO_4)_2 \cdot 12H_2O$ at −190 °C has been assigned to the ν_1 vibration, but we did not observe a band at room temperature. Until we record low-temperature spectra the reason for this difference is uncertain, but the band could be a component of ν_3 arising from partial dehydration of the sample in the cryostat.

The assignment of the remaining ν_2 bending frequency is also uncertain in the absence of reported spectra[2] of the selenate alums in the frequency range below 500 cm^{-1}. This mode

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(14) Nakamoto, K. "Infrared and Raman Spectra of Inorganic and Coordination Compounds", 3rd ed.; Wiley: New York, 1978; p 142.

is allowed in the Raman spectrum and occurs[4] at 455 cm^{-1} in $CsAl(SO_4)_2 \cdot 12H_2O$. Like the ν_1 mode it is infrared forbidden in tetrahedral symmetry and hence would be weak in the alum system. The weak band at 445 cm^{-1} observed in our infrared spectra is invariant to changes of the trivalent metal ion in the cesium alums and can probably be assigned as ν_2, but it does shift with change in the monovalent cation. This point will be discussed further below.

Water Vibrations. Distinguishing among the so-called "external" modes of the M^I and M^{III} coordinated waters and internal vibrations of the M^I and M^{III} coordination spheres is the principal purpose of this work. Following Adams[15] we will assume that, for each coordination sphere, the external wag vibration, ρ_w, occurs at a higher frequency than the rock mode, ρ_r, and that the twist mode is weak in the infrared. Excluding these twist modes, there are eight infrared active vibrations, comprising the wag and rock of both M^{III} and M^I waters and the antisymmetric M–O stretch and bend of the $M^{III}O_6$ and M^IO_6 coordination spheres. Examining the spectra we find six bands, in addition to the sulfate vibrations ν_3 and ν_4, or five if the 445 cm^{-1} band is assigned to the sulfate ν_2 mode. Either the missing vibrations occur at frequencies below 300 cm^{-1} or there are coincidences. Furthermore, the splitting of these modes allowed by the factor group symmetry is not observed at room temperature.

The highest frequency occurs at 932 ± 2 cm^{-1} in each of the cesium alums except that of cobalt, which has a different, α-alum, crystal structure. This band is assigned to the wag of the trivalent water, ρ^{III}. Its frequency has been observed[2] to shift by the expected 1.43:1 ratio on deuteration of both $CsGa(SO_4)_2 \cdot 12H_2O$ and $CsGa(SeO_4)_2 \cdot 12H_2O$. It is reasonable to assign it to the trivalent rather than to the monovalent water, both because such a vibration occurs at 800–825 cm^{-1} in the spectrum[6] of $[Al(H_2O)_6]Cl_3$ which does not possess monovalent cations and because of the general expectation that bonding to the trivalent metal cation will be stronger and causes the vibration to occur at higher frequency. The difference in the wagging frequency between the chloride salt[6] and the alum of $Al(H_2O)_6^{3+}$ presumably reflects stronger hydrogen bonding in the lattice of the alum. The frequency of this wagging mode is thus seen to depend strongly on the charge of the cation to which the water is coordinated but within similar structures to be almost independent of the identity of the trivalent cation.

Similar arguments are used to assign the vibration observed at 670 ± 3 cm^{-1} in the cesium alums to the rock of the trivalent water, ρ_r^{III}. It too has been observed[2] to shift by the expected ratio of 1.34:1 on deuteration of the gallium alums. Again the cesium cobalt alum of different structure has a different frequency, this time shifted to higher wavenumber, closer to those of α-alums of other monovalent cations (Table I). Again, assignment to the trivalent water rests on comparison with compounds without monovalent cations, such as $[Al(H_2O)_6]Cl_3$,[6] in which the rock occurs at frequencies about 250 cm^{-1} lower than the wag, just as observed in the alums.

The justification for the assignment of the antisymmetric stretch of the trivalent octahedron, $\nu_3(M^{III}O_6)$, is seen clearly in Figure 2 where the variation of the frequency between 500 and 600 cm^{-1} is clearly dependent on the identity of the trivalent metal ion. Similarly, the band which moves between 300 and 360 cm^{-1} is assigned to the antisymmetric bending mode, $\nu_4(M^{III}O_6)$. These bands vary somewhat with the identity of the monovalent cation (Table I) but are clearly much more sensitive to the identity of the trivalent cation. Thus the infrared active metal–ligand vibrations of the $M(H_2O)_6^{3+}$ complex can be assigned by comparing spectra of series of isomorphous or related structures containing different metal ions. This could be considered a type of "natural" metal–isotope experiment and has been used previously for the assignment of metal–ligand stretching frequencies.[16]

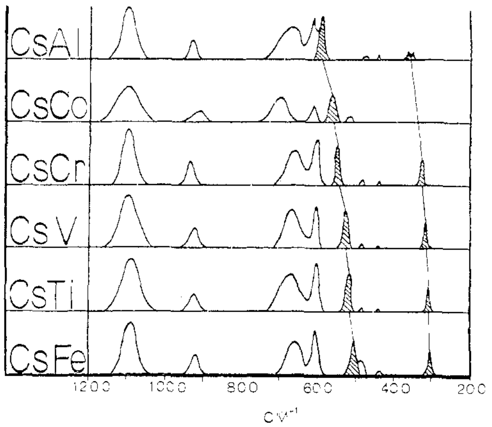

Figure 2. Comparative infrared spectra of cesium alums illustrating metal-sensitive bands.

These assignments have been confirmed by using isotope-enriched chromium alums. In the spectra of samples enriched 96.8% in ^{50}Cr or 96.4% in ^{53}Cr, only two bands shifted measurably. A shift of 5 cm^{-1} from 560 cm^{-1} in the ^{50}Cr sample to 555 cm^{-1} in the ^{53}Cr sample was observed for the ν_3 antisymmetric metal–ligand stretching mode. This can be compared with a shift of 4.2 cm^{-1} predicted from a simple diatomic harmonic oscillator calculation. A shift is also expected for the antisymmetric metal–ligand bonding mode, ν_4, and a small but measurable shift of 1 cm^{-1} was observed.

There remain the frequencies associated with the water of the monovalent cation. By analogy with the trivalent cation we might expect the external wag mode to occur at higher frequency than the rock. A band is observed at 485 ± 5 cm^{-1} in the cesium alums except that of Co^{III}, which has the different, α-alum structure, where it occurs at 523 cm^{-1}. Among the α-alums studied, this band occurs at different frequencies with different monovalent cations (Table I). If this is the wagging frequency of a water much less strongly hydrogen bonded than those of the trivalent cation, then it is probably unlikely that the band at 445 cm^{-1}, tentatively assigned above to $\nu_2(SO_4^{2-})$, is associated with the monovalent cation. This suggests that the rock $\rho_r(M^I\text{–}OH_2)$ as well as the internal vibrations of the monovalent cation occur at lower frequencies, probably below 300 cm^{-1}. Further far-infrared[5] and Raman studies will be needed to clarify their assignments.

Finally, the assignments made in this work can be compared with those previously reported in the literature. They are in agreement with those made by Petrov et al.[2] for the potassium and cesium aluminum alums, limited to frequencies above 550 cm^{-1}. A modest revision is required in the assignment of $\nu_3(M^{III}O_6)$ made for $[Al(H_2O)_6]Cl_3$.[6] The authors suggested two possibilities. Either ν_3 is coincident with $\rho_r(M^{III}\text{–}OH_2)$, which occur in the region 560–580 cm^{-1}, or it occurs at 664 or 678 cm^{-1}, positions of weak bands which were considered to be candidates for the twist mode $\rho_t(M^{III}\text{–}OH_2)$. Since ν_3 occurs at ~590 cm^{-1} in the aluminum alums, it is likely that the first choice is correct, rather than the second which the authors preferred. This revised assignment does raise some questions about their inferences on the basis of Urey–Bradley force field calculations. However, their conclusions are probably correct, for in another Raman study of $Al(H_2O)_6^{3+}$ which they did not consider, assignments were made for several

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(15) Adams, D. M.; Lock, P. J. *J. Chem. Soc. A* **1971**, 2801.

(16) Thornton, D. A. *S. Afr. J. Sci.* **1974**, *70*, 70, 110. Griffiths, G.; Thornton, D. A. *J. Mol. Struct.* **1979**, *52*, 39 and references therein.

Inorg. Chem. **1980**, *19*, 1961–1973

aluminum alums including a deuterate and a selenate.[4] The symmetric aluminum–water stretch $\nu_1(\mathrm{M^{III}{-}OH_2})$ occurs between 511 and 544 cm^{-1}, consistent with our assignment of the antisymmetric stretch ν_3 at the higher frequency of ~590 cm^{-1}. Our assignment of ν_3 does not agree with those made from infrared studies[1,3] of cesium and potassium aluminum alums. Furthermore, our assignments of the external $\mathrm{M^{III}{-}OH_2}$ modes are not in agreement with a low-temperature infrared study[1] or some aspects of the Raman study mentioned above.[4] We plan to record low-temperature infrared and Raman spectra in an attempt to resolve these differences. However, there now seems little doubt about the correctness of our assignments of the infrared active metal–ligand stretching frequencies which lie between 500 and 600 cm^{-1} for these $\mathrm{M(H_2O)_6^{3+}}$ complexes.

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Registry No. $\mathrm{CsAl(SO_4)_2{\cdot}12H_2O}$, 7784-17-0; $\mathrm{CsCo(SO_4)_2{\cdot}12H_2O}$, 19004-44-5; $\mathrm{CsCr(SO_4)_2{\cdot}12H_2O}$, 15363-19-6; $\mathrm{CsV(SO_4)_2{\cdot}12H_2O}$, 29931-99-5; $\mathrm{CsTi(SO_4)_2{\cdot}12H_2O}$, 16482-51-2; $\mathrm{CsFe(SO_4)_2{\cdot}12H_2O}$, 24389-85-3; $\mathrm{KAl(SO_4)_2{\cdot}12H_2O}$, 7784-24-9; $\mathrm{NH_4Al(SO_4)_2{\cdot}12H_2O}$, 7784-26-1; $\mathrm{KCr(SO_4)_2{\cdot}12H_2O}$, 7788-99-0; $\mathrm{NH_4Cr(SO_4)_2{\cdot}12H_2O}$, 10022-47-6; $\mathrm{Al^{III}(H_2O)_6}$, 15453-67-5; $\mathrm{Co^{III}(H_2O)_6}$, 15275-05-5; $\mathrm{Cr^{III}(H_2O)_6}$, 14873-01-9; $\mathrm{V^{III}(H_2O)_6}$, 21374-21-0; $\mathrm{Ti^{III}(H_2O)_6}$, 17524-20-8; $\mathrm{Fe^{III}(H_2O)_6}$, 15377-81-8.

Contribution from the School of Chemical Sciences, University of East Anglia, Norwich, United Kingdom,
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the Institute of Inorganic Chemistry of the University of Turin, Turin, Italy, and
the Department of Industrial and Engineering Chemistry of the Swiss Federal Institute of Technology, ETH, Zurich, Switzerland

Comparative Infrared and Raman Spectroscopic ν(CO) Study of $\mathrm{Ru_3(CO)_{12}}$, $\mathrm{Os_3(CO)_{12}}$, Their Mixed Crystals, and the Mixed Triangulo Cluster Carbonyls $\mathrm{Ru_2Os(CO)_{12}}$ and $\mathrm{RuOs_2(CO)_{12}}$[1a]

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Received September 7, 1979

High-resolution infrared and Raman spectra ν(CO) of the species $\mathrm{M}_n\mathrm{M'}_{3-n}\mathrm{(CO)_{12}}$ (M, M′ = Ru, Os; n = 0, 1, 2, or 3) are reported. The species $\mathrm{Ru_2Os(CO)_{12}}$ and $\mathrm{RuOs_2(CO)_{12}}$ were, for the first time, prepared in a spectroscopically pure state for these studies. Data on ^{13}CO-enriched $\mathrm{Ru_3(CO)_{12}}$ and $\mathrm{Os_3(CO)_{12}}$ are also presented. A detailed ν(CO) vibrational analysis, using the rotational parameter method, has been performed on $\mathrm{Ru_3(CO)_{12}}$, where overtone and intensity data have been used to augment fundamental frequencies and enable a definitive assignment. Intensity data were also used in the analysis on $\mathrm{Os_3(CO)_{12}}$; the analyses of the $\mathrm{Ru_2Os}$ and $\mathrm{RuOs_2}$ species used fundamental frequency data only. The average CO force constant has the same value (16.66 mdyn/Å) for each of the four compounds. Further, in this series individual equatorial and axial CO stretching force constants are characteristic of the metal atom involved and almost independent of the particular chemical species. All geminal interaction constants increase regularly from $\mathrm{Ru_3(CO)_{12}}$ to $\mathrm{Os_3(CO)_{12}}$, contributing, in part, to the spread in frequencies observed in passing from the triruthenium to the triosmium compound. The vibrational coupling between CO groups on different metal atoms is very significant so that it is clearly inappropriate to use a local symmetry approach to the analysis of the ν(CO) spectra of these compounds.

Introduction

During the past 15 years there have been many detailed studies of the vibrational spectra of metal carbonyls and their derivatives in the ν(CO) region. Although the majority of these have been confined to monomeric species, some detailed analyses have also been carried out in bi- and polynuclear carbonyls.[2] Some of us have recently reported detailed infrared studies of some tri- and tetranuclear species which have indicated that the combined use of frequency, band intensity, and isotopic data enables a definitive analysis to be carried out.[3,4] These studies have revealed that within a CO-factored force field, interaction constants between CO groups on adjacent atoms can be of the same order of magnitude as those between geminal CO groups. This observation is pertinent to the question of the extent of correlation of the motion between carbonyl groups on a metal surface, a topic of relevance to the understanding of the metal-surface-catalyzed reactions of CO.

The present paper is concerned with a detailed vibrational study of the trimetallo dodecacarbonyls of basic D_{3h} symmetry. The complex nature of the problems encountered in this work required for their solution the use of a variety of techniques, a situation which stimulated collaboration between several groups. The present paper is the product of the combined efforts of four laboratories; some of the more specific results obtained and the methods of analysis used are the subject of separate papers.

Vibrational spectroscopic studies on the triruthenium and triosmium dodecacarbonyls have been reported rather sporadically over the past few years; studies on $\mathrm{Os_3(CO)_{12}}$ have been more common than those on its ruthenium analogue. The first, rather sketchy, report was that of Beck and Lottes,[5] but the paper of Huggins, Flitcroft, and Kaesz,[6] describing an infrared study of $\mathrm{Os_3(CO)_{12}}$, was the first paper in which band assignments were made. Although, as we shall show, these assignments were correct on important points, the fact that

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(1) (a) To be considered as part 20 of the series "Solid-State Studies" by S. F. A. Kettle and co-workers and part 22 of the series "Infrared Spectroscopic Studies of Metal Carbonyl Compounds" by G. Bor and co-workers. For parts 19 and 21, respectively, see ref 16 and 30. (b) Laboratory for Chemistry and Technology of the Radioelements of CNR. (c) Swiss Federal Institute of Technology, ETH. (d) University of East Anglia. (e) University of Turin.

(2) For reviews see: (a) M. L. Haines and M. H. B. Stiddard, *Adv. Inorg. Chem. Radiochem.*, **12**, 53 (1969); (b) P. S. Braterman, "Metal Carbonyl Spectra", Academic Press, London, New York, San Francisco, 1975; (c) P. S. Braterman, *Struct. Bonding (Berlin)*, **26**, 1 (1976); (d) S. F. A. Kettle, *Top. Curr. Chem.*, **71**, 111 (1977).

(3) G. Bor, G. Sbrignadello, and F. Marcati, *J. Organomet. Chem.*, **46**, 357 (1972).

(4) G. Bor, G. Sbrignadello, and K. Noack, *Helv. Chim. Acta*, **58**, 815 (1975).

(5) W. Beck and K. Lottes, *Chem. Ber.*, **94**, 2578 (1961).

(6) D. K. Huggins, N. Flitcroft, and H. D. Kaesz, *Inorg. Chem.*, **4**, 166 (1965).