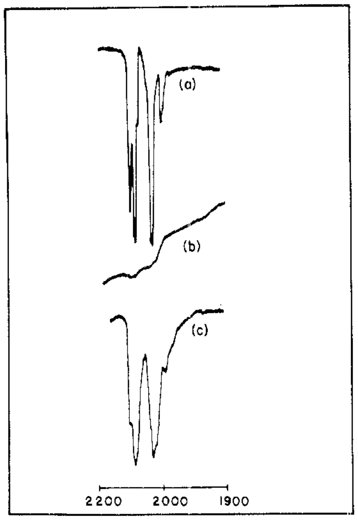

Figure 2. Ir spectra in the ν(CO) region of (a) solid $Rh_2(CO)_4Cl_2$ as Nujol mull, (b) $Rh_2(CO)_4Cl_2$ supported on Vycor after exposure to air for more than 1 day, and (c) the material obtained after exposing fully decarbonylated dimer to CO for 1 hr.

under conditions which remove oxygen from an alumina surface. The presence of this adsorbed oxygen was demonstrated by exposure of a sample to $^{18}O_2$, evacuation to remove physisorbed oxygen, and then exposure to CO. Substantial quantities of $C^{16}O^{18}O$ were formed along with lesser amounts of $C^{18}O_2$.

In order to determine whether other compounds would exhibit similar behavior and to see whether the reaction of small clusters to form larger ones was facile on the alumina surface, we studied $Rh_4(CO)_{12}$ and $Rh_2(CO)_4Cl_2$ under conditions similar to those described above. Both compounds adsorb out of alkane solvents onto the surface where they are fully decarbonylated in a short period of time. Exposure to an atmosphere of CO then produces a deep violet material with a ν(CO) spectrum identical with that in Figure 1b. The ν(CO) spectrum progresses gradually through the Figure 1b–e decarbonylation sequence upon exposure to air. In addition, $Rh_6(CO)_{16}$ can be extracted into refluxing chloroform from the violet fully carbonylated form. The alumina surface apparently acts as a very effective catalyst for the conversion of these two compounds to $Rh_6(CO)_{16}$ under an atmosphere of CO. This parallels the solution behavior in which both $Rh_2(CO)_4Cl_2$ and $Rh_4(CO)_{12}$ can be converted to $Rh_6(CO)_{16}$[11-13] under strongly basic conditions. This suggests that the strongly basic nature of the alumina surface hydroxyl groups is at least partially responsible for the course of these surface reactions.

These results on alumina surface contrast sharply with our observations using silica and Vycor support materials. All three rhodium carbonyls appear to undergo physical adsorption or crystallization onto silica surfaces where the ir spectra remain virtually identical with those of the free solids for days if the samples are maintained at room temperature. A notable exception is the system $Rh_2(CO)_4Cl_2$ on Vycor. Dramatic color changes ensue upon exposure to oxygen and the ν(CO) spectrum disappears although no new bands are observed during this decarbonylation. Under exposure to CO the color and ir spectrum typical of the dimer return with no apparent conversion to the hexanuclear carbonyl; this again contrasts with the behavior on the alumina surface. These spectral changes are shown in Figure 2.

Our studies also suggest that initiation of the observed alumina-catalyzed reaction is sensitive to the manner by which adsorption onto the alumina surface is achieved. Several samples for which deposition occurred by evaporation of a saturated chloroform solution over alumina showed none of the behavior described above. The ν(CO) spectrum was simply that of crystalline $Rh_6(CO)_{16}$ and the spectrum remained unchanged for days or weeks. Only carefully controlled adsorption out of a subsaturated solution, presumably as a monolayer or less, led to the behavior described above. It also occurred that these reactions only took place when at least a substantial fraction of the alumina adsorbent was in the γ phase. Pure β-trihydrate and α-phase samples failed to initiate the decarbonylation reactions.

These studies show that interesting reactions of metal carbonyls are catalyzed by oxide surfaces and that the exact course of the reaction is very sensitive to the type of surface involved. This is consistent with the observations of Parkyns[1] for nickel carbonyl on silica and alumina. Studies of supported catalysts derived from molybdenum hexacarbonyl[2-6] have already suggested that metal carbonyls can be used reproducibly to form supported metal catalysts by mild heating in vacuo. Our results suggest that the proper choice of metal carbonyl and oxide support may form decarbonylated metal clusters by simple room-temperature oxidation. Mild reduction conditions might then succeed in forming very active catalyst systems consisting essentially of uniform size metal clusters of just a few atoms. Synthetic and catalytic applications of these oxide-supported metal cluster carbonyls are deserving of further study.

Acknowledgment. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

Registry No. $Rh_6(CO)_{16}$, 28407-51-4; $Rh_4(CO)_{12}$, 19584-30-6; $Rh_2(CO)_4Cl_2$, 14523-22-9; Al_2O_3, 1344-28-1.

References and Notes

(1) N. D. Parkyns, *Proc. Int. Congr. Catal.*, **3**, 194 (1965).
(2) E. S. Davie, D. A. Whan, and C. Kemball, *J. Catal.*, **24**, 272 (1972).
(3) R. F. Howe, D. E. Davidson, and D. A. Whan, *J. Chem. Soc., Faraday Trans. 1*, **68**, 2266 (1972).
(4) R. F. Howe and I. R. Leith, *J. Chem. Soc., Faraday Trans. 1*, **69**, 1967 (1973).
(5) J. Smith, R. F. Howe, and D. A. Whan, *J. Catal.*, **34**, 191 (1974).
(6) A. Brenner and R. L. Burwell, *Proc. Int. Symp. Relat. Heterogeneous Homogeneous Catal. Phenom.*, in press.
(7) J. P. Collman, L. S. Hagedies, M. P. Cooke, J. R. Norton, G. Dolcetti, and D. N. Marquardt, *J. Am. Chem. Soc.*, **94**, 1789 (1972).
(8) R. H. Grubbs, C. Gibbons, L. C. Kroll, W. D. Bonds, Jr., and C. H. Brubaker, Jr., *J. Am. Chem. Soc.*, **95**, 2373 (1973).
(9) K. Iwatate, S. R. Dasgupta, R. L. Schneider, G. C. Smith, and K. L. Watters, submitted for publication.
(10) J. A. McCleverty and G. Wilkinson, *Inorg. Synth.*, **8**, 214 (1966).
(11) P. Chini and S. Martinengo, *Inorg. Chim. Acta*, **3**, 315 (1969).
(12) P. Chini and S. Martinengo, *Chem. Commun.*, 251 (1968).
(13) P. Chini and S. Martinengo, *Inorg. Chim. Acta*, **3**, 299 (1969).

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Resonance Raman Spectra of Superoxide-Bridged Binuclear Complexes. $[(CN)_5CoO_2Co(CN)_5]^{5-}$ and $[(NH_3)_5CoO_2Co(NH_3)_5]^{5+}$ [1]

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Received October 7, 1974 AIC406937

Resonance Raman spectroscopy affords the potential of elucidating both vibrational and electronic transitions, since their coupling produces resonance enhancement of Raman bands.[2,3] The technique offers particular promise in biological systems,[4] where vibrations of chromophoric groupings can be

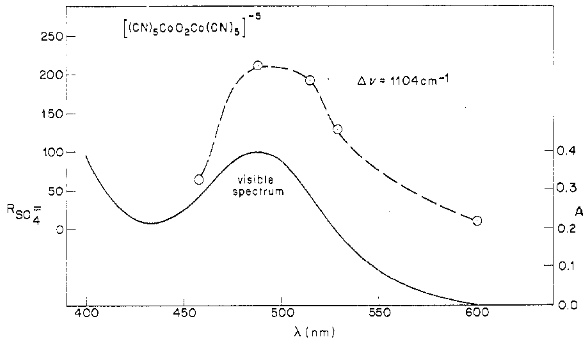

Figure 1. Comparison of the visible absorption spectrum (*A* = absorbance) of $[(CN)_5Co(O_2)Co(CN)_5]^{5-}$ (Na^+ salt) with intensities (○) of the 1104-cm^{-1} aqueous solution Raman band. $R_{SO_4^{2-}}$ is the molar intensity divided by the molar intensity of the 983-cm^{-1} (ν_1) band of SO_4^{2-}, added as an internal standard. A rotating cell was employed.

monitored in a macromolecular matrix. Recently, the oxygen-carrying proteins hemoglobin,[5] hemerythrin,[6] and hemocyanin[7] have been investigated by this method. In the case of hemerythrin, enhanced Raman bands at 844 and 500 cm^{-1}, excited in an absorption band which is generally thought to arise from $O_2^{2-} \rightarrow Fe(III)$ charge transfer, could be conclusively assigned, via $^{18}O_2$ isotope shifts, to O–O and Fe–O stretching, respectively. The ν_{O-O} frequency is typical for peroxide and confirms previous suggestions[8] that the electronic structure of oxyhemerythrin is well represented by $Fe^{3+}–O_2^{2-}–Fe^{3+}$. In hemocyanin, a band at 742 cm^{-1} (704 cm^{-1} for $^{18}O_2$) is assigned to peroxide stretching, in resonance with a 575-nm $O_2^{2-} \rightarrow Cu(II)$ charge-transfer band.

Many peroxide- and superoxide-bridged binuclear Co(III) complexes have been prepared and characterized.[9,10] We have explored the solution Raman spectra of two members of the latter, superoxide groups: $[(CN)_5Co(O_2)Co(CN)_5]^{5-}$ and $[(NH_3)_5Co(O_2)Co(NH_3)_5]^{5+}$. The X-ray structures reveal a trans bridging superoxide group in the nitrate and sulfate salts of the latter.[10,11] The electronic spectrum of $[(CN)_5Co(O_2)Co(CN)_5]^{5-}$ shows a band of moderate intensity (~745 M^{-1} cm^{-1}) centered at 486 nm, and more intense bands at higher energy. The assignment of the 486-nm band is controversial;[10,12] perturbed d–d,[13,14] localized superoxide,[15] and $Co^{3+} \rightarrow O_2^-$ charge-transfer[16] transitions have been suggested.

Results and Discussion

Blue or green Ar^+ laser excitation of dilute (7 m*M*) solutions of $[(CN)_5Co(O_2)Co(CN)_5]^{5-}$ (Na^+ salt) gave only two readily observable Raman bands, at 1104 and 493 cm^{-1}. The former frequency is typical for superoxide[17] and must be assigned to ν_{O-O}. The 493-cm^{-1} band is then assigned to Co–O stretching by analogy with M–O stretching frequencies found in hemerythrin[7] and in monomolecular oxygen adducts.[18] The intensity of the 1104-cm^{-1} band was measured relative to the nearby 983-cm^{-1} (ν_1) band of SO_4^{2-}, added as an internal standard (the 493-cm^{-1} band could not be so measured because of interference by a SO_4^{2-} band at 450 cm^{-1}) at several excitation wavelengths of the Ar^+ laser as well as at a longer wavelength provided by a tunable dye (Rhodamine 6G) laser. As shown in Figure 1, the 1104-cm^{-1} intensity tracks the 486-nm absorption band. Since O–O stretching is clearly coupled to the electronic transition centered at 486 nm, we conclude that the latter must involve a significant change in the occupancy of superoxide orbitals; assignment to a largely d–d transition seems unlikely on this basis.

The 486-nm band is shifted[10,14] to much lower energy, 672 nm (ϵ ~927 M^{-1} cm^{-1}) in $[(NH_3)_5Co(O_2)Co(NH_3)_5]Cl_5$, while a weaker band ($\epsilon$ ~309 M^{-1} cm^{-1}) appears at 480 nm.

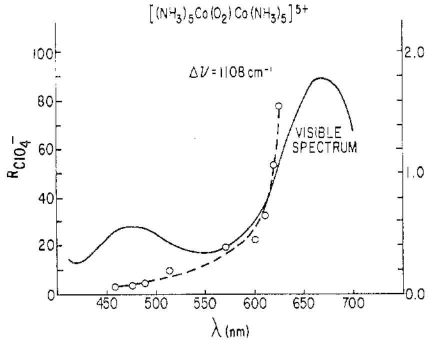

Figure 2. Comparison of the visible absorption spectrum of $[(NH_3)_5Co(O_2)Co(NH_3)_5]^{5+}$ with intensities of the 1108-cm^{-1} (○) Raman band obtained in 0.1 *M* HCl solution. $R_{ClO_4^-}$ is the molar intensity divided by the molar intensity of the 935-cm^{-1} (ν_1) band of ClO_4^-, added as an internal standard.

The Raman spectrum of dilute (2.2 m*M*) solutions in 0.1 *N* HCl, using 0.1 *M* ClO_4^- (ν_1 935 cm^{-1}) as internal standard, again shows bands at characteristic Co–O and O–O stretching frequencies, 500 and 1108 cm^{-1}. Solid $[(NH_3)_5Co(O_2)Co(NH_3)_5]Cl_5$ gives a Raman spectrum (obtained with a spinning cell) displaying the O–O stretching band at 1119 cm^{-1}, in agreement with a recent report.[19]

The excitation profile for the 1108-cm^{-1} superoxide stretching band of $[(NH_3)_5Co(O_2)Co(NH_3)_5]^{5+}$ (Figure 2) shows no peak corresponding to the 480-nm visible transition but rises continuously toward lower energy as the excitation wavelength approaches the 672-nm transition. This behavior parallels the relative enhancement with the 486-nm band of the cyanide complex and supports the correlation of the two transitions as previously proposed.[10,14]

Experimental Section

$Na_5[(CN)_5Co(O_2)Co(CN)_5]$ and $[(NH_3)_5Co(O_2)Co(NH_3)_5]Cl_5$ were prepared as described in ref 9.

Raman spectra were recorded with excitation from a Coherent Radiation CR-5 Ar^+ laser and a Spectra Physics dye laser (Rhodamine 6G) pumped by the Ar^+ laser. The spectrometer is based on a Spex 1401 double monochromator and ITT FW 130 photomultiplier with dc amplification. A Spex sample rotator was used in obtaining some of the spectra. Relative intensities were determined by measuring band areas.

Registry No. $Na_5[(CN)_5Co(O_2)Co(CN)_5]$, 54844-30-3; $[(NH_3)_5Co(O_2)Co(NH_3)_5]Cl_5$, 12526-59-9.

References and Notes

(1) We thank Dr. Vincent Miskowski and Professor Harry B. Gray for helpful discussions. This work was supported by NIH Grant GM 13498 and NSF Grant GP 41008X.
(2) T. G. Spiro and T. C. Strekas, *Proc. Natl. Acad. Sci. U.S.A*, **69**, 2622 (1972).
(3) L. A. Nafie, M. Pézolet, and W. L. Peticolas, *Chem. Phys. Lett.*, **20**, 563 (1973).
(4) T. G. Spiro in "Chemical and Biological Applications of Lasers", C. B. Moore, Ed., Academic Press, New York, N.Y., 1974, Chapter 2.
(5) T. G. Spiro and T. C. Strekas, *J. Am. Chem. Soc.*, **96**, 338 (1974); H. Brunner, A. Mayer, and H. Sussner, *J. Mol. Biol.*, **70**, 153 (1972); T. Yamamoto, G. Palmer, D. Gill, I. T. Salmeen, and L. Rimai, *J. Biol. Chem.*, **248**, 5211 (1973).
(6) J. B. R. Dunn, D. F. Shriver, and I. M. Klotz, *Proc. Natl. Acad. Sci. U.S.A.*, **70**, 2582 (1973).
(7) J. S. Loehr, T. B. Freedman, and T. M. Loehr, *Biochem. Biophys. Res. Commun.*, **56**, 570 (1974).
(8) K. Garbett, D. W. Darnell, I. M. Klotz, and R. J. P. Williams, *Arch. Biochem. Biophys.*, **103**, 419 (1969); K. E. Van Holde, *Biochemistry*, **6**, 93 (1967); H. B. Gray, *Adv. Chem. Ser.*, **No. 100**, 365 (1971).
(9) R. Davies, M. Mori, A. G. Sykes, and J. A. Weil, *Inorg. Synth.*, **12**, 197–214 (1970).
(10) A. G. Sykes and J. A. Weil, *Prog. Inorg. Chem.*, **13**, 1–106 (1970).
(11) R. E. Marsh and W. P. Schaefer, *Acta Crystallogr., Sect. B*, **24**, 246 (1968).
(12) J. S. Valentine and D. V. Valentine, Jr., *J. Am. Chem. Soc.*, **93**, 1111 (1971).

(13) M. Linhard and M. Weigel, *Z. Anorg. Allg. Chem.*, **308**, 254 (1961).
(14) J. Barrett, *Chem. Commun.*, 874 (1968).
(15) K. Garbett and R. D. Gillard, *J. Chem. Soc. A*, 1725 (1968).
(16) V. Miskowski, J. Robbins, I. M. Treitel, and H. B. Gray, to be submitted for publication.
(17) F. J. Blunt, P. J. Hendra, and J. R. Mackenzie, *Chem. Commun.*, 278 (1969).
(18) R. W. Horn, E. Weissberger, and J. P. Collman, *Inorg. Chem.*, **9**, 2367 (1970).
(19) T. Shibahara, *J. Chem. Soc., Chem. Commun.*, 864 (1973).

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High-Conductivity Solid Electrolytes. Tropyllium Iodide–Silver Iodide System

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Received October 23, 1974 AIC407283

Since the discovery[1-3] of the family of high-conductivity solid electrolytes $\mathrm{MAg_4I_5}$ (M = K, Rb, $\mathrm{NH_4}$), we have carried out an extensive search for high ionic conductivity in other AgI double-salt systems. We have previously reported the discovery of many compounds of high ionic conductivity in the systems QI–AgI, where Q^+ is an ammonium ion[4-6] or a sulfonium ion.[7] The high Ag^+ mobility in these compounds has been attributed to the unique crystal structures characterized by face-sharing iodide polyhedra, forming channels of Ag^+ sites through the structure, and by a large excess of vacant Ag^+ sites in the unit cell.[8-11]

In this paper we report our investigation of the tropyllium iodide ($\mathrm{C_7H_7I}$)–silver iodide system, the first examination of a stable carbonium ion system.

Experimental Section

Using the method of Kursanov and Vol'pin[12] for the preparation of tropyllium chloride, a stirred mixture of 41 g of $\mathrm{PCl_5}$ in 500 ml of $\mathrm{CCl_4}$ was treated dropwise with 9 g of cycloheptatriene in 50 ml of $\mathrm{CCl_4}$. The system was protected by a $\mathrm{CaCl_2}$ tube. After addition of the triene was complete, the heavy slurry was stirred for 2 hr at room temperature and was then filtered through a coarse frit. The collected filtrate was cooled in Dry Ice and 20 ml of $\mathrm{H_2O}$ was added dropwise with stirring. Much heat and HCl were evolved. After warming to 25°, 50 ml of 55% HI was added to the solution of $\mathrm{C_7H_7Cl}$, followed by 200 ml of acetone. Bright red crystals of $\mathrm{C_7H_7I}$ separated, were collected, washed with acetone, and stored in vacuo.

Mallinckrodt reagent grade AgI was used without further purification. The AgI–$\mathrm{C_7H_7I}$ compositions were prepared by the paste preparation procedure previously described.[4] The measurement of the density of the electrolytes has also been described.[4] The conductivities were measured using the cell Ag, $\mathrm{RbAg_4I_5}$–sample–Ag, $\mathrm{RbAg_4I_5}$ as previously reported.[4,13] All measurements were made at 22°.

Results

The experimentally determined densities and specific conductivities are shown in Table I. Contact resistances[13] were not determined; the reported values for the specific conductivities therefore represent a lower limit. Our experience[4] indicates that the corrected values would be 5–8% higher.

Discussion

The observed maximum in specific conductivity around 80–85 mol % of AgI, while not as sharp as that observed in other systems,[4,6-8] indicates that at least one compound with specific conductivity greater than that of AgI is formed in this system. More work would be necessary to establish the exact stoichiometry of the conductive compound (or compounds). The fact that the electrochemical cell Ag–$\mathrm{C_7H_7I{\cdot}4AgI}$–C, $\mathrm{(CH_3)_4NI_9}$ has the correct potential of 0.63 V indicates that the conduction is primarily ionic, rather than electronic.[14]

Table I. Density and Specific Conductivity in the Tropyllium Iodide–Silver Iodide System

Mol % of AgI	Density, g/cm^3	Specific conductivity, (ohm cm)$^{-1}$
75	4.16	5.04×10^{-3}
80	4.42	5.84×10^{-3}
85	4.69	5.78×10^{-3}
90	4.97	5.30×10^{-3}
95	5.33	1.94×10^{-3}
100	5.75	4.00×10^{-4}

The highest conductivity we have observed for onium iodide–silver iodide compounds is 0.06 (ohm cm)$^{-1}$ (e.g., for diethyldimethylammonium[4] and quinuclidinium[6]); the maximum conductivity shown in Table I is an order of magnitude less, but still an order of magnitude greater than the conductivity of pure AgI. The inorganic compound $\mathrm{RbAg_4I_5}$ has a specific conductivity of 0.26 (ohm cm)$^{-1}$.

The work presented here supports our previous conclusions[4,6,7] that there are a multitude of QI–AgI solid electrolytes exhibiting high ionic conductivity and that the Q^+ ion, whether ammonium, sulfonium, or, as in this case, carbonium, serves merely to stabilize a structure through which the Ag^+ ion can move freely.[15] The most important characteristic of the Q^+ ion seems to be its size, rather than its composition and structure.[4,6]

Acknowledgment. This investigation was supported in part by the North American Rockwell Corp. Independent Research and Development Program.

Registry No. AgI, 7783-96-2; $\mathrm{C_7H_7I}$, 1316-80-9.

References and Notes

(1) B. B. Owens and G. R. Argue, *Science*, **157**, 308 (1967).
(2) J. N. Bradley and P. D. Greene, *Trans. Faraday Soc.*, **62**, 2069 (1966).
(3) J. N. Bradley and P. D. Greene, *Trans. Faraday Soc.*, **63**, 424 (1967).
(4) B. B. Owens, *J. Electrochem. Soc.*, **117**, 1536 (1970).
(5) B. B. Owens, *Adv. Electrochem. Electrochem. Eng.*, **8**, 1–61 (1971).
(6) B. B. Owens, J. H. Christie, and G. T. Tiedeman, *J. Electrochem. Soc.*, **118**, 1144 (1971).
(7) J. Christie, B. Owens, and G. Tiedeman, Abstracts, 146th Meeting of the Electrochemical Society, New York, N.Y., Oct 14, 1974, No. 20.
(8) S. Geller, *Science*, **157**, 310 (1967).
(9) S. Geller and M. D. Lind, *J. Chem. Phys.*, **52**, 5854 (1970).
(10) S. Geller, *Science*, **176**, 1016 (1972).
(11) S. Geller and B. B. Owens, *J. Phys. Chem. Solids*, **33**, 1241 (1972).
(12) D. N. Kursanov and M. E. Vol'pin, *Dokl. Akad. Nauk SSSR*, **113**, 339 (1957); *Chem. Abstr.*, **51**, 14572*e* (1957).
(13) B. B. Owens and G. R. Argue, *J. Electrochem. Soc.*, **117**, 898 (1970).
(14) C. Wagner, *Proc. Int. Comm. Electrochem. Thermodyn. Kinet.*, **7**, 361 (1957).
(15) H. Wiedersich and S. Geller, "The Chemistry of Extended Defects in Non-Metallic Solids", L. Eyring and M. O'Keefe, Ed., North-Holland Publishing Co., Amsterdam, 1970, pp 629–650.

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Interaction of Cobalt(II)–Glycylglycine Chelates with Molecular Oxygen. Species in Solution[1a]

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Received November 7, 1974 AIC407743

The nature of the factors governing the properties of cobalt oxygen complexes has recently elicited considerable interest.[2-4]