C_{4v}) frameworks and correlation tables, shows that only the C_{4v} geometry for cation D is likely to account for this result. Thus, this pentacoordinated species would consist of a square-based pyramid.

Conclusion

Following our previous work on $AlBr_3/CH_3CN$ and using the same procedure, we have identified the main species that are formed by the solvolysis of $AlCl_3$ in CH_3CN.[35] This

---

(35) Since the submission of this paper for publication, a paper has appeared which is concerned with the Al NMR study of dilute CH_3CN solutions of $AlCl_3$, $AlBr_3$, and AlI_3.[36] Chemical shift values are consistent with our data, if we take into account a constant difference of 1.2 ppm. In the 1 M concentration range, their spectrum is quite similar to that which we have obtained with $R = 19.7$. At lower concentrations, their spectra exhibit some features which are at the same positions and look like the bands that we have found to correspond to hydrated species.[24] Nevertheless, their assignment of the sharp line at −7.5 ppm to the *cis*-$AlCl_3(CH_3CN)_3$ complex is unambiguous, and this result provides an accuate basis for the calculation of the pairwise parameters, without any assumption regarding the stereochemistry of the C cation. The modified δ parameters are $\delta_{NN} = -2.83$, $\delta_{NCL} = -0.33$ and $\delta_{ClCl} = 0.59$. This basis leads to the calculated chemical shifts of 33.96 ppm for $Al(CH_3CN)_6^{3+}$, −23.96 ppm for $AlCl(CH_3CN)_5^{2+}$ −16.33 ppm for *cis*-$AlCl_2(CH_3CN)_4^+$, and −13.96 ppm for *trans*-$AlCl_2(CH_3CN)_4^+$ and to the assignment of our C band to the *trans*-$AlCl_2(CH_3CN)_4^+$ cation.

system is more complex than the first one. The use of the concept of "mean cationic charge" is of the greatest interest in the study of systems that contain several ionic species. Our work also demonstrates the use of high-field NMR spectrometers for the study of complex solutions: the 23.45-MHz spectra do not make possible a self-consistent analysis of all the equilibria involved in the $AlCl_3/CH_3CN$ mixtures. The study of $AlCl_3$ dissolved in binary mixtures is in progress by using the above results and will be published later.

(36) F. W. Wehrli and S. Wehrli, *J. Magn. Reson.*, **44**, 197 (1981).

Contribution from the Todd Wehr Chemistry Building, Marquette University, Milwaukee, Wisconsin 53233

Infrared and Resonance Raman Spectra of Molecular Oxygen Adducts of [*N*,*N*'-Ethylenebis(acetylacetoniminato)]cobalt(II)

MAREK W. URBAN, YASUOMI NONAKA, and KAZUO NAKAMOTO*

The infrared spectra of base-free $Co(acacen)O_2$ (acacen = *N*,*N*'-ethylenebis(acetylacetoniminato) anion) were measured with matrix cocondensation techniques. Its O_2 stretching frequency, $\nu(O_2)$ (1146 cm^{-1}), is much lower than that of previously reported $Co(TPP)O_2$ (1278 cm^{-1}). This low-frequency shift is interpreted as indicating that the negative charge on O_2 increases markedly in going from $Co(TPP)O_2$ to $Co(acacen)O_2$. The resonance Raman spectra of the O_2 adducts of $Co(acacen)$ were measured in CH_2Cl_2 containing a variety of base ligands at low temperatures. Both axial (base) and in-plane ligand effects on $\nu(O_2)$ are noted: $Co(acacen)O_2$ (1146 cm^{-1}) vs. $Co(acacen)(1\text{-MeIm})O_2$ (1017 cm^{-1}) and $Co(TPP)(1\text{-MeIm})O_2$ (1142 cm^{-1}) vs. $Co(acacen)(1\text{-MeIm})O_2$ (1017 cm^{-1}). The $\nu(O_2)$ decreases linearly as the base strength of the axial ligand (B) increases in the $[Co(acacen)B]_2O_2$ series. Two different straight-line relationships were obtained, one for pure σ-donor ligands and one for σ- as well as π-donor ligands.

Introduction

Previously, we[1] prepared the "base-free" $Co(TPP)O_2$ (TPP = tetraphenylporphyrinato anion) via a matrix cocondensation reaction and located its O_2 stretching frequency ($\nu(O_2)$) at 1278 cm^{-1}, which is much higher than that of "superoxo" adducts (1195–1130 cm^{-1}).[2] For example, this frequency is higher by 136 cm^{-1} than that of $Co(TPP)(1\text{-MeIm})O_2$ (1-MeIm = 1-methylimidazole) (1142 cm^{-1}).[3] We attributed this large shift of $\nu(O_2)$ to the effect of the base ligand (1-MeIm) which tends to increase the negative charge on the O_2 via σ and π donation. A similar base ligand effect was noted for $[Co(salen)]_2O_2$ (1011 cm^{-1})[4] vs. $[Co(salen)(py)]_2O_2$ (888 cm^{-1})[5] (salen = *N*,*N*'-ethylenebis(salicylideniminato) anion).

In the present investigation, we focused our attention on the in-plane (chelating) ligand effect on $\nu(O_2)$. A previous in-

vestigation[6] of cobalt(II) Schiff base complexes studied the axial (base) and in-plane ligand effects by measuring equilibrium constants for oxygen adduct formation and redox potentials. One observation made was that the formation constant (K_{O_2} (mm^{-1})) for the reaction $Co(\text{chelate})(\text{py}) + O_2 \rightleftharpoons Co(\text{chelate})(\text{py})O_2$ was much larger for $Co(acacen)(\text{py})$ (−0.28) than for $Co(p\text{-MeO(TPP)})(\text{py})$ (−3.1) (acacen = *N*,*N*'-ethylenebis(acetylacetoniminato) anion; *p*-MeO(TPP) = tetrakis(*p*-methoxyphenyl)porphyrinato anion). Also, the potential (volt vs. SCE) for the anodic wave $Co(II) \rightarrow Co(III)$ was much higher for the former (−0.59) than for the latter (−0.23).
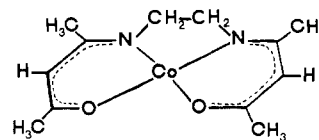
These results were interpreted as indicating that, relative to acacen, *p*-MeO(TPP) delocalizes more electron density from

---

(1) Kozuka, M.; Nakamoto, K. *J. Am. Chem. Soc.* **1981**, *103*, 2162.
(2) Jones, R. D.; Summerville, D. A.; Basolo, F. *Chem. Rev.* **1979**, *79*, 139.
(3) Jones, R. D.; Budge, J. R.; Ellis, P. E., Jr.; Linard, J. E.; Summerville, D. A.; Basolo, F. *J. Organomet. Chem.* **1979**, *181*, 151.
(4) Suzuki, M.; Ishiguro, T.; Kozuka, M.; Nakamoto, K. *Inorg. Chem.* **1981**, *20*, 1993.
(5) Nakamoto, K.; Suzuki, M.; Ishiguro, T.; Kozuka, M.; Nishida, Y.; Kida, S. *Inorg. Chem.* **1980**, *19*, 2822.

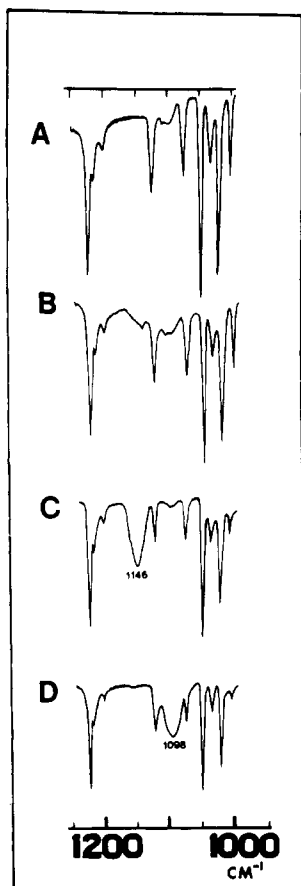(6) Carter, M. J.; Rillema, D. P.; Basolo, F. *J. Am. Chem. Soc.* **1974**, *96*, 392.

Figure 1. IR spectra of cocondensation products of Co(acacen) with O$_2$ in Ar at ~16 K: (A) without O$_2$, (B) with Ar/^{16}O$_2$ (100/1), (C) with Ar/^{16}O$_2$ (10/1), and (D) with Ar/^{18}O$_2$ (10/1).

cobalt into the in-plane ligand π system, resulting in a less negative O$_2$ moiety in the adduct and a lower O$_2$ affinity by the complex. This makes it of particular interest to compare the ν(O$_2$) of Co(TPP)O$_2$ and Co(TPP)(1-MeIm)O$_2$ with those of Co(acacen)O$_2$ and Co(acacen)(1-MeIm)O$_2$, respectively.

Experimental Section

The literature method[7] was used to prepare and purify Co(acacen). The gases ^{16}O$_2$ (99.99%, Matheson), ^{18}O$_2$ (99.88%, Monsanto Research), and Ar (99.9995%, Matheson) were used without further purification. The solvent (CH$_2$Cl$_2$) and base ligands (CNpy, aniline, py, 1-MeIm, benzylamine, and *n*-BuNH$_2$) were purchased from Aldrich Chemical Co. and purified before use.

The "base-free" Co(acacen)O$_2$ was prepared by the matrix cocondensation technique; Co(acacen) was vaporized from a Knudsen cell at ~430 K and cocondensed with ^{16}O$_2$ or ^{18}O$_2$ diluted in Ar on a CsI window which was cooled to ~16 K by a CTI Model 21 closed-cycle helium refrigerator. IR spectra were measured on a Beckman Model 4260 infrared spectrophotometer using a 25 cm^{-1}/in. chart expansion and 5 cm^{-1}/min chart speed. Rotation–vibration bands of standard molecules and polystyrene film bands were used to calibrate the frequency reading.

Resonance Raman (RR) spectra of solutions containing Co(acacen) and a base ligand were measured in a Raman Dewar cell designed in our laboratory. In a typical experiment, 2 mmol of Co(acacen) was dissolved in 10 mL of CH$_2$Cl$_2$ containing 3% base ligand. The temperature of the solution was controlled by organic slushes. The spectra were measured on a Spex Model 1401 double monochromator using the 514.5-nm line of a Spectra-Physics Model 164-08 Ar ion laser. Detection was made by using a cooled RCA C31034 photomultiplier in conjunction with a Spex digital photometer system. Calibration of frequency reading was made by using plasma lines from the Ar ion laser.
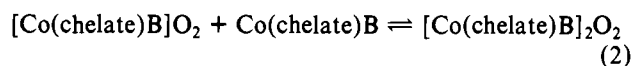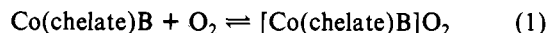
(7) Everett, G. W., Jr.; Holm, R. H. *J. Am. Chem. Soc.* **1966**, *88*, 2442.

Results and Discussion

IR Spectrum of Co(acacen)O$_2$. Trace A of Figure 1 shows the IR spectrum of Co(acacen) in an Ar matrix at ~16 K. When Co(acacen) was codeposited with ^{16}O$_2$ diluted in Ar (1/100) at the same temperature, no new bands were observed except for the weak hump near 1146 cm^{-1} (trace B). However, a new strong band appeared at 1146 cm^{-1} when the concentration of ^{16}O$_2$ in Ar was increased to the 1/10 ratio (trace C). As is seen in trace D, this band was shifted to 1098 cm^{-1} by the ^{16}O$_2$–^{18}O$_2$ substitution. Thus, the bands at 1146 and 1098 cm^{-1} have been assigned to the ν(O$_2$) of Co(acacen)^{16}O$_2$ and its ^{18}O$_2$ analogue, respectively. The weak hump seen in trace B grew into a strong band at 1146 cm^{-1} by warming the matrix to ~25 K. Apparently, the warmup process increased the rate of formation of the O$_2$ adduct via diffusion in Ar matrices.

As stated before, Co(TPP)^{16}O$_2$ prepared by the same technique exhibited its ν(O$_2$) at 1278 cm^{-1} (ν(^{18}O$_2$), 1209 cm^{-1}).[1] Thus the ν(O$_2$) has shifted from 1278 to 1146 cm^{-1} in going from Co(TPP)O$_2$ to Co(acacen)O$_2$. Similar to the case of the axial ligand effect, we attribute this large shift (132 cm^{-1}) to the increasing negative charge on the O$_2$ in going from Co(TPP)O$_2$ to Co(acacen)O$_2$. In general, the larger the electron density on the Co atom, the more the electron density drifts from the Co atom to the O$_2$. This observed shift in ν(O$_2$) is in good accord with the earlier report[6] that the anodic potential is higher (Co(II) is more easily oxidized) for Co(acacen)(py) than for Co(*p*-MeO(TPP))(py). (Here, we assume that the potential for Co(TPP)(py) does not differ appreciably from that of Co(*p*-MeO(TPP))(py).)

RR Spectra of Co(acacen)(base)O$_2$. Previous studies[1] showed that the coordination of 1-MeIm to Co(TPP)O$_2$ shifts the ν(O$_2$) from 1278 to 1142 cm^{-1}. If a shift of similar magnitude occurs for Co(acacen)O$_2$, the ν(O$_2$) of Co(acacen)(1-MeIm)O$_2$ could be as low as 1010 cm^{-1}, which is much lower than the designated "superoxo" range of 1195–1130 cm^{-1}.[2] Although the strong IR bands at 1140–1120 cm^{-1} of Co(acacen)(base)O$_2$-type compounds[8] were tentatively assigned to ν(O$_2$), it is noted that these crystals are thermally unstable and their IR spectra are complicated. For this reason it was decided to examine the RR spectra of the O$_2$ adducts in solution where they are stable at low temperatures. Furthermore, RR spectroscopy simplifies their vibrational spectra markedly since only the ν(O$_2$), ν(CoO), and several Co(N$_2$O$_2$) core vibrations are enhanced when the laser frequency is tuned in the Co–O$_2$ CT transition.[4,5]

Equilibria 1 and 2 are established when a Co(II) chelate

$$\text{Co(chelate)B} + \text{O}_2 \rightleftharpoons [\text{Co(chelate)B}]\text{O}_2 \qquad (1)$$

$$[\text{Co(chelate)B}]\text{O}_2 + \text{Co(chelate)B} \rightleftharpoons [\text{Co(chelate)B}]_2\text{O}_2 \qquad (2)$$

dissolved in a nonaqueous solvent absorbs oxygen in the presence of a base (B). As demonstrated previously[9] Co(J-en) (J-en = *N*,*N'*-ethylenebis(2,2-diacetylethylideniminato) anion), such solutions generally exhibit the ν(O$_2$) of both 1:1 and 1:2 (O$_2$/metal) adducts. Trace A of Figure 2 shows the RR spectrum ((514.5-nm excitation) of Co(acacen) in CH$_2$Cl$_2$ containing 3% py at −35 °C. The solvent (CH$_2$Cl$_2$) bands are marked by asterisks. Two bands at 1126 and 1032 cm^{-1} are due to Co(acacen)py, and one band at 991 cm^{-1} is due to py. As is seen in trace B, a new band appeared at 808 cm^{-1} when the solution was saturated with ^{16}O$_2$. This band can be assigned to the ν(O$_2$) of the 1:2 adduct, since it is in the range

(8) Crumbliss, A. L.; Basolo, F. *J. Am. Chem. Soc.* **1970**, *92*, 55; *Science (Washington, D.C.)* **1969**, *164*, 1168.

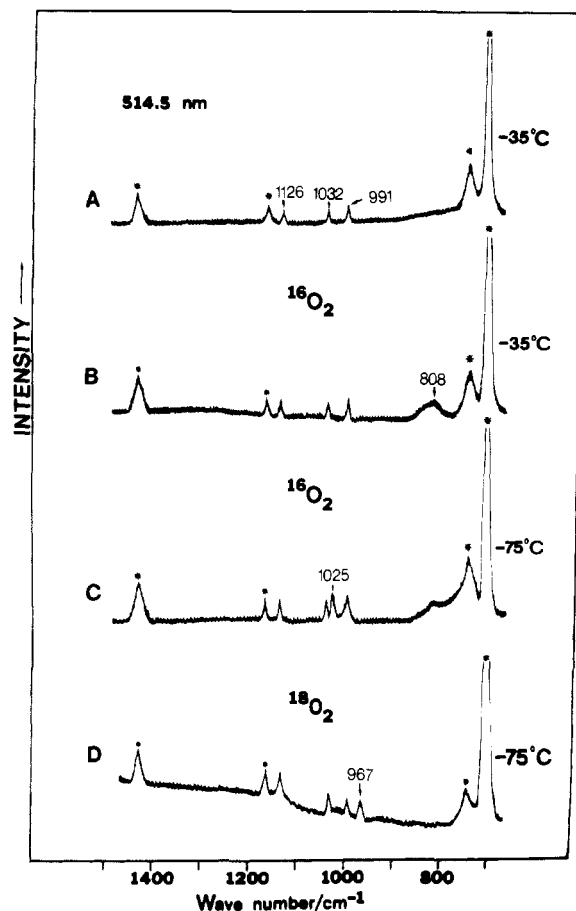(9) Kozuka, M.; Suzuki, M.; Nishida, Y.; Kida, S.; Nakamoto, K. *Inorg. Chim. Acta* **1980**, *45*, L111.

Figure 2. RR spectra of Co(acacen) in CH_2Cl_2 containing 3% pyridine (514.5-nm excitation): (A) without O_2 (−35 °C), (B) with $^{16}O_2$ (−35 °C), (C) with $^{16}O_2$ (−75 °C), and (D) with $^{18}O_2$ (−75 °C). Solvent bands are marked with asterisks, and the band at 991 cm^{-1} is due to pyridine. Co(acacen)py exhibits two bands at 1126 and 1032 cm^{-1}.

for peroxo 1:2 adducts (885–790 cm^{-1})^2 and since it is shifted to a lower frequency by the $^{16}O_2$–$^{18}O_2$ substitution.

When the solution was cooled to −75 °C, the band at 808 cm^{-1} became weaker, and a new band appeared at 1025 cm^{-1} (see trace C of Figure 2). The latter band was shifted to 967 cm^{-1} by the $^{16}O_2$–$^{18}O_2$ substitution (trace D). Thus, we assign the 1025-cm^{-1} band to the $\nu(O_2)$ of the 1:1 adduct Co(acacen)(py)O_2. The above observation is consistent with the previous findings that the 1:1 adducts are more stable at lower temperatures[6] and are formed more rapidly than are the 1:2 adducts.[10] The 1025-cm^{-1} band shifts to 1017 cm^{-1} when 1-MeIm is used as a base ligand (Figure 3C). These results show that replacement of TPP by acacen causes a low-frequency shift of 125 cm^{-1} for $\nu(O_2)$ in complexes of the type Co(chelate)(1-MeIm)O_2.

It is apparent that the $\nu(O_2)$ of "base-free" Co(chelate)O_2 shifts markedly to a lower frequency with coordination of a ligand at the axial position. The magnitude of this shift depends upon the nature of the ligand. For the [Co(salen)B]$_2O_2$ series, the $\nu(O_2)$ of the py complex (888 cm^{-1}) is lower than that of the pyO (pyridine *N*-oxide) complex (910 cm^{-1}).[5] Since py (pK_a = 5.20)[11] is a much stronger base than is pyO (pK_a = 0.8),[11] it follows that py would give a greater electron density on cobalt than would pyO. This is in accord with the lower $\nu(O_2)$ for the py system where there is more electron transfer to the O_2 moiety in the adduct. However, electron drift from
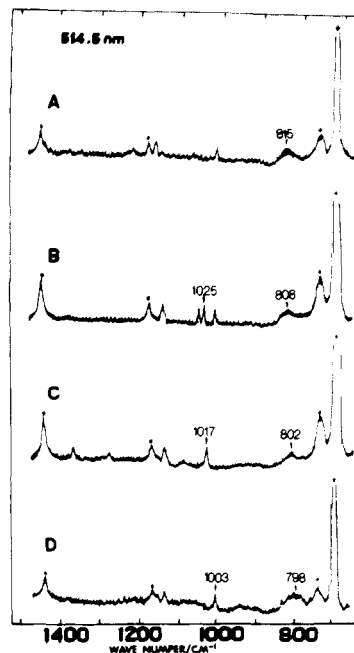
(10) Stynes, D. V.; Stynes, H. C.; Ibers, J. A.; James, B. R. *J. Am. Chem. Soc.* **1973**, *95*, 1142.

(11) Perrin, D. D. "Dissociation Constants of Organic Bases in Aqueous Solutions"; Butterworths: London, 1965.

Figure 3. RR spectra of Co(acacen) in CH_2Cl_2 containing 3% base ligand which was saturated with O_2 (514.5-nm excitation, −75 °C): (A) CNpy, (B) py, (C) 1-MeIm, and (D) *n*-BuNH$_2$.
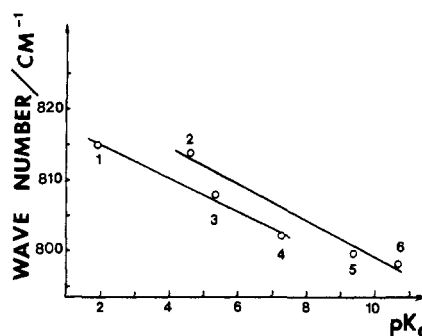

Figure 4. Plot of $\nu(O_2)$ vs. pK_a of the conjugated acid of a base for 1:2 complexes: (1) CNpy, (2) aniline, (3) py, (4) 1-MeIm, (5) benzylamine, and (6) *n*-BuNH$_2$.

Table I. O_2 Stretching Frequencies of Molecular Oxygen Adducts of Co(acacen) in CH_2Cl_2 Containing Base Ligands

base	p$K_a{}^b$	$\nu(O_2),^c$ cm^{-1}	
		1:1 adduct	1:2 adduct
CNpy	1.85	*a*	815
aniline	4.60	*a*	814
py	5.20	1025	808
1-MeIm	7.20	1017	802
benzylamine	9.33	1016	800
n-BuNH$_2$	10.61	1003	798

a The basicity is too low to form a 1:1 adduct in solution. *b* pK_a of the conjugated acid. *c* O_2 stretching frequency.

a base to the O_2 may occur via σ and/or π donation.[6] In an attempt to study these two effects, we have measured the RR spectra of Co(acacen) in CH_2Cl_2 containing type A bases (*n*-BuNH$_2$, benzylamine and aniline) which are pure σ donors and type B bases (CNpy, py and 1-MeIm) which may act as both σ and π donors.

Figure 3 shows the RR spectra of Co(acacen) in CH_2Cl_2 containing some of these bases. Except for the CNpy (4-cyanopyridine) and aniline systems, we were able to observe the $\nu(O_2)$ of both 1:1 and 1:2 adducts. Table I lists all the $\nu(O_2)$ observed in this work. Figure 4 plots the $\nu(O_2)$ of the 1:2 adduct against the pK_a of the conjugated acid of the base. It is seen that the $\nu(O_2)$ shifts linearly to a lower frequency

as the pK_a of the conjugated acid of the base increases. This trend may hold for the 1:1 adduct series although not enough points are available to confirm it. Furthermore, type A and B bases give different straight lines with the type B line shifted to a lower position on the ordinate scale. The difference between these two slopes may indicate the magnitude of π contribution to the basicity (hence the lowering of $\nu(O_2)$). Similar results have been obtained for the 1:2 adducts of Co(J-en).[12]

According to the spin-pairing model of the Co–O$_2$ bond,[13] the amount of negative charge on the O$_2$ depends upon the nature of the in-plane (chelating) and axial (base) ligands. In fact, our studies indicate that the $\nu(O_2)$ of Co(chelate)(B)O$_2$ complexes can vary over a wide range from 1278 (Co(TPP)O$_2$) to 1003 cm^{-1} (Co(acacen)(n-BuNH$_2$)O$_2$). This range is much wider than that previously defined[2] and is contrary to the

statement[13] that "the values of $\nu(O_2)$ are relatively insensitive to the metal, the ligand field strength, and the strength of dioxygen binding". However, the latter conclusion is based in part on tentative $\nu(O_2)$ assignments which we have now shown to be in error. Clearly, more data must be obtained before a general statement can be made regarding the sensitivity of $\nu(O_2)$ to the metal and the ligand field strength. This is particularly true for the O$_2$ adducts of metalloporphyrins since thus far very limited data are available on their $\nu(O_2)$.

Registry No. Co(acacen)O$_2$, 56295-08-0; Co(acacen)(py)O$_2$, 42742-62-1; Co(acacen)(1-MeIm)O$_2$, 80186-61-4; Co(acacen)(benzylamine)O$_2$, 80186-62-5; Co(acacen)(n-BuNH$_2$)O$_2$, 80186-63-6; [Co(acacen)(CNpy)]$_2$O$_2$, 80186-64-7; [Co(acacen)(aniline)]$_2$O$_2$, 80186-65-8; [Co(acacen)(py)]$_2$O$_2$, 80186-66-9; [Co(acacen)(1-MeIm)]$_2$O$_2$, 80186-67-0; [Co(acacen)(benzylamine)]$_2$O$_2$, 80186-68-1; [Co(acacen)(n-BuNH$_2$)]$_2$O$_2$, 80186-69-2; Co(acacen), 36802-26-3.

(12) Nakamoto, K.; Nonaka, Y.; Ishiguro, T.; Urban, M. W.; Suzuki, M.; Kozuka, M.; Nishida, Y.; Kida, S., submitted to *J. Am. Chem. Soc.*

(13) Drago, R. S.; Corden, B. B. *Acc. Chem. Res.* **1980**, *13*, 353 and references therein.

Spectroscopy at Very High Pressures. 36. An Infrared Study of Spin-State Equilibria in Some Iron(II) Complexes

DAVID M. ADAMS,*[1a] GARY J. LONG,*[1b] and ALAN D. WILLIAMS[1a]

The complexes cis-[Fe(o-phen)$_2$X$_2$] (X = I, NCS, NCSe, and N$_3$) have been studied under hydrostatic pressures of up to 40 kbar in a diamond-anvil cell. The spectra of these, and of the related complexes [M(o-phen)$_3$]$^{n+}$, are interpreted by deriving the skeletal modes from those of the free-ligand translations and rotations. The spectrum of the iodide is consistent with the presence of a mixture of high-spin and low-spin isomers in roughly equal proportions at 30 kbar, but the azido complex appears to be almost entirely converted to low-spin at this pressure. The new data for the thiocyanato and isocyanato complexes indicate that the spin-state transitions occur near 8 and 6 kbar, respectively, lower than previous estimates based upon samples under shear stress, and are quite sharp.

Introduction

The spin configurations of certain transition-metal complexes can be affected by change of temperature and/or pressure.[2,3] Among the best known examples are the materials cis-[Fe(o-phen)$_2$X$_2$], where X is an anionic ligand.[4] The behavior under pressure of members of this series has been followed by using Mössbauer, optical,[5] and far-IR spectroscopies.[6] Changes in IR absorption associated with passing through the high- to low-spin transition on cooling have also been reported.[7,8]

We have examined the far-IR absorption spectra of the compounds with X = I, NCS, NCSe, and N$_3$ under high pressure in a diamond-anvil cell (dac). The iodide and azide complexes have not been studied previously by high-pressure IR spectroscopy. They have proved to be valuable in reaching an understanding of the spectra of the whole series. We have repeated Ferraro and Takemoto's work[6] on the NCS and NCSe complexes using hydrostatic pressure conditions (i.e., with a gasket between the two diamonds); in their work the

dac was used without a gasket, and the samples were therefore subjected to a large shear stress. Further, we wished to find whether the IR results substantiated the rather curious spin-equilibria vs. pressure data of Fisher and Drickamer,[5] which suggest that increase of pressure first brings about partial conversion of high-spin material to low-spin and that with further pressure increase there is partial reversion to high-spin behavior.

Experimental Section

The compounds were prepared by standard methods. The dac and the technique for high-pressure far-IR spectroscopy have been described elsewhere.[9] Samples were contained within molybdenum gaskets initially 0.1 mm thick with a central hole of 0.4-mm diameter. The pressure-transmitting liquid within the gasket hole was Nujol: this does not interfere in the far-IR but it freezes under pressure at about 13 kbar. At higher pressures an increasingly large shear component is thus applied to the samples but this is very small compared with that developed in the sample in a nongasketed dac.

The pressure-transmitting fluid contained the sample to be studied, plus a small chip of ruby, which acted as the pressure calibrant.[10,11] The ruby R lines were followed by using a Raman spectrometer. Far-IR spectra were obtained by using a Beckman-RIIC FS-620 Fourier spectrometer. As the energy transmitted through a hole 0.4

(1) (a) University of Leicester. (b) University of Missouri—Rolla.

(2) Ferraro, J. R. *Coord. Chem. Rev.* **1979**, *29*, 1.

(3) Ferraro, J. R.; Long, G. J. *Acc. Chem. Res.* **1975**, *8*, 171.

(4) König, E.; Madeja, K. *Inorg. Chem.* **1967**, *6*, 48.

(5) Fisher, D. C.; Drickamer, H. G. *J. Chem. Phys.* **1971**, *54*, 4825.

(6) Ferraro, J. R.; Takemoto, J. H. *Appl. Spectrosc.* **1974**, *28*, 66.

(7) Takemoto, J. H.; Hutchinson, B. *Inorg. Nucl. Chem. Lett.* **1972**, *8*, 769.

(8) Takemoto, J. H.; Hutchinson, B. *Inorg. Chem.* **1973**, *12*, 705.

(9) Adams, D. M.; Payne, S. J.; Martin, K. *Appl. Spectrosc.* **1973**, *27*, 377.

(10) Piermarini, G. J.; Block, S.; Barnett, J. D.; Forman, R. A. *J. Appl. Phys.* **1975**, *16*, 2774.

(11) Adams, D. M.; Appleby, R.; Sharma, S. K. *J. Phys. E* **1976**, *9*, 1140.