*Inorganica Chimica Acta*, 45 (1980) L185–L187
©Elsevier Sequoia S.A., Lausanne – Printed in Switzerland

# $\pi \rightarrow \pi^*$ Transitions in Terminally Coordinated Superoxides and Nitrogen to Cobalt(III) Charge Transfer Spectra

A. B. P. LEVER[†] and S. R. PICKENS

*Department of Chemistry, York University, Downsview (North York), Ont. M3J 1P3, Canada*

Received May 26, 1980

There has been considerable interest in recent years in the study of the electronic structures of metal dioxygen complexes as an aid to understanding oxygen to metal binding in oxymetalloproteins, oxygen–metal interactions in oxidation and oxygenation catalysis and oxygen binding to metal surfaces such as in fuel cell electrodes [1]. While considerable success has been achieved in interpreting the charge transfer electronic spectra of superoxocobalt(III) complexes [1–3], little has been said concerning the location of the $\pi \rightarrow \pi^*$ transition of terminally coordinated superoxide.

The hydroperoxy radical in the gas phase has a band at about 47.6 kK (210 nm) corresponding to this transition [4]. Superoxide present as a doped impurity in alkali halide crystals has a broad absorption band at 40 kK (250 nm) with a shoulder at 44 kK (225–230 nm) [5].

Miskowski *et al.* [2] have assigned shoulders in the spectra of the dinuclear bridging superoxocobalt(III) complexes $[Co_2(NH_3)_{10}O_2]^{5+}$ and $[Co_2(CN)_{10}O_2]^{5-}$ at 44. kK (225 nm, $\epsilon = 10{,}000$–$20{,}000\ M^{-1}cm^{-1}$) to the $\pi_v \rightarrow \pi_v^*$ $(O_2^-)$ transition. In neither case was there any other clearly defined band present in the 39–48 kK range (33–50 kK in the case of the decammine).

We have previously reported [3] spectra for mononuclear terminal superoxo complexes of the type $[Co(s\text{-}R_2en)_2XO_2]^{n+}$ where s-R$_2$en is a symmetric N,N′-dialkylethylenediamine, R = Me, Et, and n = 1 when X = Cl, Br, and n = 2 when X = solvent (MeOH, EtOH or $CH_3CN$). We have further investigated these complexes with special attention to the higher energy regions of the spectra. In addition to absorption features due to halogen to cobalt(III) charge transfer (see Table I), we see a band at 47.2 ± 0.8 kK (212 ± 4 nm, $\epsilon = 12{,}000\ M^{-1}\ cm^{-1}$ assuming complete oxygenation at 200 K), common to all these complexes.

Before assigning this to the anticipated $\pi \rightarrow \pi^*$ superoxo transition, we consider the possibility that nitrogen to cobalt(III) charge transfer could occur in this region. In Table I we report the electronic spectra of some cobalt (III) complexes with UV transparent amine ligands. Halogen to cobalt(III) charge transfer bands are assigned according to previous studies with which we concur [6]. On this basis it is clear that the nitrogen to cobalt(III) charge transfer band must appear above 52 kK in *trans*-$[Co(en)_2Br_2]^+$, no other band being present in the range 35–52 kK, and appears likewise to be above 50 kK in both *cis* and *trans*-$[Co(en)_2Cl_2]^+$. A band is observed quite distinctly at 47.5 kK in the spectrum of $[Co(en)_3]^{3+}$.

There is also a high energy shoulder at 48 kK on the edge of the Cl → Co charge transfer band in $[Co(NH_3)_5Cl]^{2+}$. In agreement with previous assignments [7] of cobalt(III) pentammine halides, these bands are assigned to nitrogen to cobalt(III) charge transfer. Thus such charge transfer absorption is expected near 47–50 kK, but appears to lie above 50 kK in the bis(ethylenediamine) derivatives.

Some peroxo complex data are also shown in Table I. It is clear that the closed shell peroxide should not exhibit a $\pi \rightarrow \pi^*$ transition. These complexes do exhibit bands at about 50 kK reasonably assigned as nitrogen to cobalt(III) charge transfer.

Given that the superoxo complexes contain the bis(ethylenediamine) unit, we conclude that by analogy with the data mentioned above, the band at 47.2 kK is most probably assignable to the missing $\pi \rightarrow \pi^*$ $(O_2^-)$ transition.

In summary, and for currently a very limited data set, we conclude that the $\pi \rightarrow \pi^*$ transition of a terminally bound superoxo cobalt(III) complex does appear blue shifted relative to the bridging superoxodicobalt(III) complex, which in turn is blue shifted relative to $KO_2$. This is consistent with a model in which interaction of superoxide with a cobalt $d_\pi$ orbital serves to elevate the $O_2^-$ $\pi_v^*$ orbital in energy while for geometric and energetic reasons leaving the $\pi_v$ orbital largely unaffected [1]. The fact that this elevation of the $\pi_v^*$ orbital is greater in the case of the mononuclear complex is supported by the observation of a blue shift of some 5 kK in the $d_\pi \rightarrow \pi_v^*$ metal to ligand charge transfer band in $[Co)s\text{-}Me_2en)_2Cl)O_2^-)]^+$ relative to $[Co_2(NH_3)_{10}(O_2^-)]^{5+}$, a shift that cannot readily be accounted for by the expected difference in $d_\pi$ energies between the two complexes [3]. The greater elevation of the $O_2^-$ $\pi_v^*$ level in the mononuclear complex may be related to the larger Co–O–O bond angle generally found for the terminal compared with the bridging complexes [8], such that the $\pi_v^*$ orbitals (tilted behind the oxygen atoms) will be directed more toward the cobalt $d_\pi$ orbital. However further experimental data are desirable before a firm conclusion can be drawn. The differences under discussion are quite small.

---

[†] Author to whom correspondence should be addressed.

TABLE I. Electronic Spectra of Cobalt(III) Complexes[a].

| COMPLEX | $^1A_{1g} \rightarrow {}^1E_g$ | $^1A_{1g} \rightarrow {}^1T_{1g}$ or $^1A_{1g} \rightarrow {}^1A_{2g}$ | $^1A_{1g} \rightarrow {}^1T_{2g}$ | $\chi_\pi \rightarrow$ CoCT[b] | $\chi_\sigma \rightarrow$ CoCT[b] | $\pi \rightarrow \pi^*$ ($O_2^-$) | N → CoCT |
|---|---|---|---|---|---|---|---|
| $[Co(en)_3]^{3+}$ | | 21.47(99)[c] | 29.50(87)[c] | | | | 47.5(21,400) |
| | | 21.43(88.9) | 29.49(81.4) | | | | |
| $[Co(NH_3)_5Cl]^{2+}$ | 18.73(51)[c] | | 27.44(52)[c] | | 44.05(20,000)[c] | | ~48(~10,000)sh |
| | 18.7 (>41)[d] | 21.35(12)[c] | 27.4 (>36)[d] | 36.50(450)[c] | 44.0 (13,400) | | |
| *cis*-$[Co(en)_2Cl_2]^+$ | | 18.8 (83)[c,e] | 25.58(73)[c,e] | 32.02(590)[c] | 41.67(19,000)[c] | | >50 |
| | | 18.7 (>72)[d] | 25.9 (>66)[d] | 32.4 (>400)[d] | 43.9 (>8,100)[d] | | |
| *trans*-$[Co(en)_2Cl_2]^+$ | 16.0 (70)[c,e] | 22.1 (30)[c,e] | 25.95(37)[c,e] | 32.48(800)[c,e] | 41 (20,000)[c,e] | | >50[c] |
| | | 22.2 (29) | 24.8 (38) | 32.8 (1,600) | 40.2 (7,900) | | >50 |
| *trans*-$[Co(en)_2Br_2]^+$ | 15.21(54)[c] | 21.68(31)[c] | | 28.10(2,200)[c] | 34.60(22,000)[c] | | >52 |
| | 15.25(47) | ~21.2 (~10)sh | | 28.3 (2,200) | 34.6 (22,000) | | |
| $[\{Co(en)_2(NH_3)\}_2(O_2^{2-})]^{4+}$ | | | | | 33.2 (4,000) | | ~50.0(18,200) |
| $[\{Co(s\text{-}Me_2en)_2H_2O\}_2(O_2^{2-})]^{4+}$ | | | | 27.8 (310)[f] | 31.4 (630)[f] | | ~51.5(23,000)[f] |
| $[Co(s\text{-}Et_2en)_2MeOH(O_2^-)]^{2+}$ | | 20.4 (24)[f] | | | 29.8 (1,200)[f] | 47.2(12,000)[f] | >50 |

[a] Frequencies of band maxima given in kK (=1000 cm$^{-1}$). Extinction coefficients given in parentheses as $M^{-1}$ cm$^{-1}$.

[b] $X = Cl^-$, $Br^-$, $O_2^{2-}$ or $O_2^-$. In the case of $O_2^-$ $\chi_\pi$ should be taken as $\pi_v^*$ and $\chi_\sigma$ as $\pi_h^*$ in ref. 2. In the case of $O_2^{2-}$ the distinction is somewhat less well defined, but may be taken as $\pi_a^*$ and $\pi_b^*$ of ref. 1 respectively.

[c] From ref. 12. [d] Extinction coefficient not measured exactly. [e] Mean of the reported values. [f] These extinction coefficients should be taken as lower limits due to possibly incomplete oxygenation.

## Experimental

Somewhat more than usual detail concerning the preparation and purification of the complexes, and the collection of electronic spectroscopic data, is presented, because of the care which is necessary to obtain definitive data at high energies near 45 - 52 kK. Care was also taken to ensure that the spectra reported in Table I are independent of the nature of the counter anion.

### *Preparation of the Complexes*

The complexes $Co(en)_2Cl_2$ [9], and $[Co(NH_3)_5Cl]Cl_2$ [10] were prepared by the literature methods. $Co(en)_3(ClO_4)_3$ was prepared by adding an almost saturated solution of sodium perchlorate (2g/ml) to an almost saturated solution of the recrystallised $Co(en)_3Cl_3$ [11] at room temperature. The electronic spectrum of the perchlorate is identical to that of the chloride up to 50 kK. *Cis*- and *trans*-$[Co(en)_2Cl_2]Cl$ were prepared from pure crystalline $[Co(en)_2CO_3]Cl$ [9]. *Trans*-$[Co(en)_2Br_2]Br$ was similarly prepared from $[Co(en)_2CO_3]Br$ [9]. *Trans*-$[Co(en)_2Br_2]ClO_4$ was prepared from the above by the method of Linhard and Weigel [12]. The spectrum of the perchlorate resembles that of the bromide except that the perchlorate spectrum (in 0.1 *M* perchloric acid) may be followed up past 50 kK whereas the bromide (in 0.1 *M* hydrobromic acid) cuts off at *ca.* 45 kK. $[Co_2(en)_4(NH_3)_2O_2](ClO_4)_4 \cdot 2H_2O$ was prepared from $[Co_2(NH_3)_{10}O_2](NO_3)_4 \cdot 2H_2O$ by the method of Duffy, House and Weil [13]. Spectra of the recrystallised material differed little from the original product. $[Co_2(s\text{-}Me_2en)_4(H_2O)_2O_2]^{4+}$ was prepared *in situ* at room temperature by dissolving $Co(s\text{-}Me_2en)_2Br_2$ [14] in water in the presence of air and obtaining spectra almost immediately. $[Co(s\text{-}Me_2en)_2(ROH)O_2]^{2+}$ was likewise prepared *in situ* by dissolving $Co(s\text{-}R_2en)_2X_2$ [14] (X = Cl, Br, R = Et, Me) in methanol or ethanol under nitrogen and admitting oxygen (1 atm.) at temperatures varying from $-15$ to $-70$ °C [3].

### *Electronic Spectra*

These were obtained with a Hitachi -Perkin Elmer model PE-340 microprocessor controlled spectrophotometer. The oxygen free cobalt(III) complexes were dissolved in 0.1 or 1.0 molar solutions of the acids corresponding to the uncoordinated anions, *e.g.* $Co(en)_2Cl_2$ was dissolved in 0.1 molar hydrochloric acid. The spectra were obtained using stored baselines of the pure organic solvent or dilute acid as reference. The spectra of the peroxo complexes were obtained in pure water. In all cases repeated scans were obtained to allow extrapolation to the time of mixing or dissolving. In the case of the superoxo series $[Co(s\text{-}R_2en)_2R'OH(O_2)]X_2$ recorded in pure methanol or ethanol, the spectra were essentially the same for all permutations of R and R′ and X (Cl, Br) except for variation in degree of oxygenation (*e.g.* less for R′ = Et) and some halogen coordination exhibiting weak halogen to cobalt charge transfer bands, when the solvent is ethanol [3]. Only bands common to all permutations are shown in Table I. In all cases the spectra were recorded several times to ensure accuracy and reproducibility.

## References

1 A. B. P. Lever and H. B. Gray, *Accounts Chem. Res., 11,* 348 (1978).
2 V. M. Miskowski, J. L. Robbins, I. M. Treitel and H. B. Gray, *Inorg. Chem., 14,* 2318 (1975).
3 S. R. Pickens, A. E. Martell, G. McLendon, A. B. P. Lever and H. B. Gray, *Inorg. Chem., 17,* 2190 (1978).
4 J. J. Paukert and H. S. Johnston, *J. Chem. Phys., 56,* 2824 (1972).
5 J. Rolfe, J. R. Lipsett and W. J. King, *Phys. Rev., 123,* 446 (1961).
6 G. Chottard, *Chem. Phys. Lett., 23,* 443 (1973).
7 A. W. Adamson and P. D. Fleischauer, 'Concepts of Inorganic Photochemistry', John Wiley, New York, (1975).
8 G. McLendon and A. E. Martell, *Coord. Chem. Rev., 19,* 4 (1976).
9 J. Springbørg and C. E. Schaffer, *Inorg. Synth., 14,* 63 (1973).
10 G. G. Schlessinger, *Inorg. Synth., 9,* 160 (1967).
11 J. B. Work, *Inorg. Synth., 2,* 221 (1946).
12 M. Linhard and Z. Weigel, *Z. Anorg. Allg. Chem., 271,* 101 (1952).
13 D. L. Duffy, D. A. House, and J. A. Weil, *J. Inorg. Nucl. Chem., 31,* 2053 (1969); R. Davies, M. Mori, A. J. Sykes and J. A. Weil, *Inorg. Synth., 12,* 197 (1970).
14 A. B. P. Lever and E. Mantovani, *Can. J. Chem., 51,* 1567 (1973).