EPR of the Co(II) complexes of phenanthraquinonedioxime and benzoquinonedioxime. Formation of dioxygen adducts in the solid state

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Abstract. Cobalt(II) complexes of 9,10-phenanthrenedionedioxime (pqdH$_2$) and benzoquinonedioxime (bqdH$_2$) and the doped sample, Co(pqdH)$_2$/Ni(pqdH)$_2$ were prepared and investigated by EPR. The EPR parameters, especially the small hyperfine splitting values, reveal the presence of oxygen adduct in the concentrated (undoped) samples, while the dilute (doped) sample has parameters corresponding to a $^2A_1(|z^2\rangle)$ ground state. It is proposed that the oxygen adducts are formed as intermediates, leading ultimately to the *tris*-chelate Co(III) complexes of these oximes, which however could not be isolated in pure form.

Keywords. Co(II) oximes; Co(II) dioxygen adducts; EPR.

1. Introduction

Planar Co(II) complexes have received considerable attention in the past, mainly from two different angles. Complexes of Schiff bases and related ligands have been considered as possible catalysts for the activation of molecular oxygen (Hitchman 1977; Daul *et al* 1979; Jones *et al* 1979; Smith and Pilbrow 1981; Herron 1986; Murray *et al* 1986). Monomeric dioxygen complexes are well known with this class of ligands (Jones *et al* 1979; Smith and Pilbrow 1981; Murray *et al* 1986). The oxime complexes, on the other hand, have been studied as possible models for vitamin-B$_{12}$ (Rockenbauer *et al* 1975; Jones *et al* 1979; Smith and Pilbrow 1981; Baumgarten *et al* 1987; Lopez *et al* 1986). Co(II) dioximates are more susceptible to oxidation and dioxygen complexes which could be possible intermediates in their air oxidation have not been observed so far, except in the case of vitamin-B$_{12r}$ itself (Jorin *et al* 1979). Most of the cobaloxime studies are conducted in solution. While there are several EPR studies on Co(II) complexes of Schiff bases and other N$_2$O$_2$ ligands doped in the corresponding diamagnetic Ni(II) complexes, with one exception (Lubitz *et al* 1987) the EPR studies on Co(II) dioximates are confined to frozen solutions. The Schiff base complexes generally have the highest occupied molecular orbital (HOMO) dominated by the $|yz\rangle$ component. Axial perturbation by σ-donor ligands changes the HOMO to $|z^2\rangle$ and thereby activates the complexes towards dioxygen binding. In the case of cobalt triazene-1-oxide complexes (Chacko and Manoharan 1974; Rajasekharan and Manoharan 1981) no oxygen adducts are obtained even in donor solvents implying greater separation between $|z^2\rangle$ *and* $|yz\rangle$ orbitals. Ready oxidation of Co(II) dioximates by air may mean that they have the HOMO derived from $|z^2\rangle$ orbital even in the absence of axial ligands. However, paucity of EPR data in the diamagnetic host lattices has made verification of this hypothesis difficult. In the case of cobaloxime(II),

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appreciable axial interaction occurs even in non-coordinating solvents leading to departure of magnetic parameters from those of the four coordinate complex (Baumgarten *et al* 1987). We now present EPR evidence for the formation of paramagnetic dioxygen adduct in the solid complex of Co(II) with 9,10-phenanthrenedionedioxime $(pqdH_2)$ and benzoquinonedioxime $(bqdH_2)$. It has also been possible to study $Co(pqdH)_2$ doped in the corresponding nickel complex.

2. Experimental

The ligands, $pqdH_2$ (Schmidt and Soll 1907) and $bqdH_2$ (Boyer and Ellzey 1960), were prepared according to previously reported procedures and recrystallized from methanol.

Preparation of complexes

A solution of 125 mg (2·12 mmol) of $CoCl_2·6H_2O$ in 60 ml methanol was added dropwise to a warm solution of 250 mg (1·05 mmol) of the ligand in 60 ml methanol, with constant stirring. The reddish-brown precipitate which formed immediately was stirred in solution for another hour, filtered and washed several times with hot methanol and finally with diethyl ether. The product was dried in vacuum at 80°C. It was sparingly soluble in chloroform and pyridine and could be recrystallised without decomposition from the former solvent. Based on the EPR and magnetic susceptibility data (*vide supra*) the Co(II) complex of $pqdH_2$ was formulated as a mixture of $Co(pqdH)_2O_2$ and a diamagnetic part. The elemental analysis data fit better with the formulation of the diamagnetic component as $Co(pqdH)_3$ rather than $(pqdH)_2CoO_2$ $Co(pqdH)_2$:C = 65·1, H = 3·8, N = 10·7, Co = 8·3%. $CoC_{38·5}H_{24·8}N_{5·5}$ O_6{$0·75 Co(pqdH)_3.0·25Co(pqdH)_2O_2$}} requires C = 64·1, H = 3·5, N = 10·7, Co = 8·3%. The Co(II) complex of $bqdH_2$ was not subjected to elemental analysis.

Preparation of doped samples

$Ni(pqdH)_2$ was prepared according to an earlier known procedure (Walter 1936). The doped sample, $Co/Ni(pqdH)_2$ was obtained in an analogous manner using a mixture of 95% $NiCl_2·6H_2O$ and 5% $CoCl_2·6H_2O$ as starting material. The sample contained a nominal, 1 mol % of cobalt. Attempts to dope $Co(bqdH)_2$ in $Ni(bqdH)_2$ were not successful.

Physical measurements

EPR spectra at the X-band were measured on a JEOL Fe-3X spectrometer. Measurements below room temperature were made using controlled boil-off from a liquid nitrogen cryostat. Magnetic susceptibility in the temperature range 20–295 K was measured by the Faraday method. by mounting the sample on the cold head of a closed cycle cryostat. C,H,N analysis was made on a Perkin–Elmer-240 C analyser. Cobalt was estimated by gravimetry (Basset *et al* 1982). Computer simulations of EPR spectra were made using a previously described computer program (Swarnabala and Rajasekharan 1989).

3. Results and discussion

Figure 1 shows the room temperature EPR spectrum of the cobalt complex of $pqdH_2$. There is no significant change upon cooling the sample to 120 K. The spectrum consists
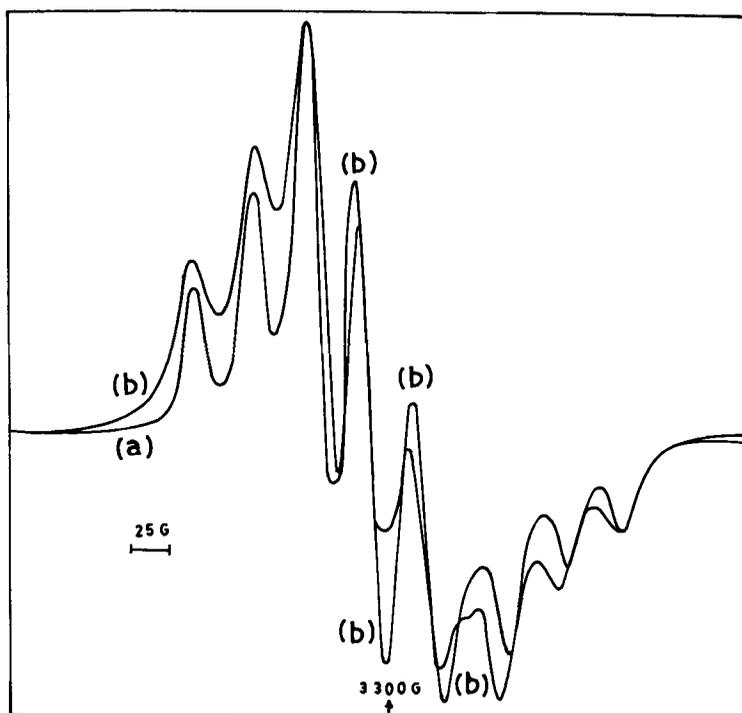
Figure 1. Polycrystalline EPR spectrum (at X-band) of the Co(II) complex of pqdH$_2$ at 298 K: (a) experimental spectrum; (b) simulated spectrum.

of signals from two distinct species, one giving rise to clearly identifiable 8 lines from ^{59}Co ($I = 7/2$) hyperfine splitting and another species which gives a strong single line at $g \sim 2$. The intensity of the latter signal varies from sample to sample. When a freshly prepared sample is suspended in water and oxygenated by bubbling air, intensities of both the signals increase initially. However, upon continued oxygenation, the intensity of the single line increases while the 8-line pattern diminishes (figure 2). The small g-anisotropy and the small ^{59}Co hyperfine splitting clearly indicate that the spectrum cannot arise from a magnetically dilute planar four-coordinate Co(II) complex. The magnetic parameters, however, can be readily understood if dioxygen of the air has added on to the axial position to give Co(pqdH)$_2$O$_2$. Compared to the dioxygen adducts of pentacoordinate Co(II) complexes ($g_\| = 2{\cdot}08$, $g_\perp = 2{\cdot}0$, $A_\| = 0{\cdot}0020$ cm^{-1}, $A_\perp = 0{\cdot}0010$ cm^{-1}, Smith and Pilbrow 1981) and vitamin-B$_{12r}$ ($g_1 = 1{\cdot}994$, $g_2 = 2{\cdot}012$, $g_3 = 2{\cdot}079$, $A_1 = -0{\cdot}0007$ cm^{-1}, $A_2 = -0{\cdot}0009$ cm^{-1}, $A_3 = -0{\cdot}0021$ cm^{-1}, Jorin *et al* 1979) the present complex has significantly lower g-anisotropy and also reduced ^{59}Co hyperfine interaction, with $g_x = 2{\cdot}018$, $g_y = 2{\cdot}011$, $g_z = 2{\cdot}009$, $A_x = 0{\cdot}0002$ cm^{-1}, $A_y = 0{\cdot}0008$ cm^{-1} and $A_z = 0{\cdot}0019$ cm^{-1}. The parameters fit a peroxy radical description more ($g = 2{\cdot}02$, Biskupic and Valko 1975) than a superoxide one ($g = 2{\cdot}08$, Kanzing and Cohen 1959) for the coordinated O$_2$. Recently oxygenation of a polymer bound Co(II) porphyrin was reported (Kamachi *et al* 1989). In this case the O$_2$-complex gave a single $g = 2{\cdot}01$ EPR line. The hyperfine splitting was not resolved. While the peroxy or superoxo designation does not necessarily imply complete charge transfer, it is likely
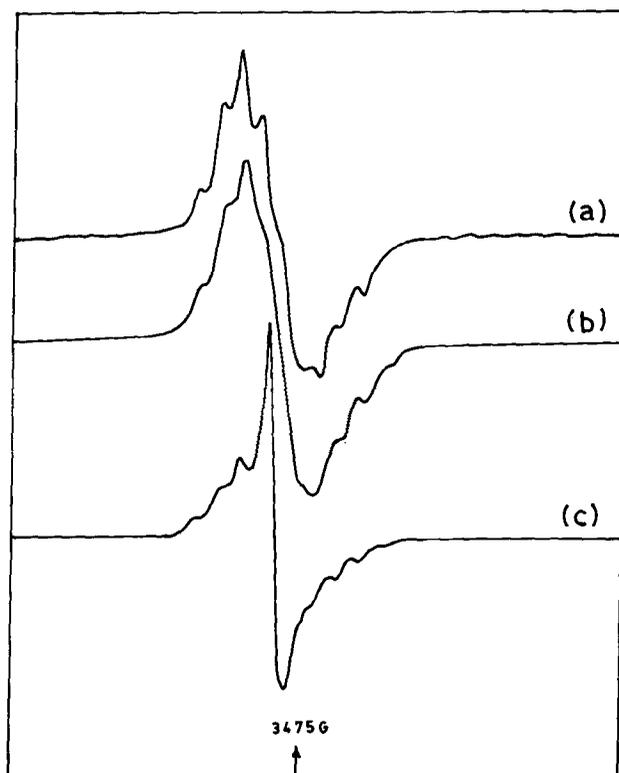
Figure 2. Polycrystalline EPR spectrum (at X-band) of the Co(II) complex of pqdH$_2$ formed under different conditions: (a) freshly prepared (unrecrystallised) sample, (b) sample suspended in water and aerated for 24 hours, (c) air bubbled during the preparation process itself.

that the O–O bond is considerably weakened upon coordination with the dioximato complex. Unfortunately no definite conclusion can be drawn from the infrared spectrum because of the interference from ligand vibrations in the 850–1150 cm^{-1} region. In a recent study (Gupta *et al* 1989) a similar kind of EPR spectrum was obtained for 4-NHCOCH$_3$C$_6$H$_4$CH$_2$Co(dmgH)$_2$py (dmgH$_2$ = dimethylglyoxime, py = pyridine) in frozen dichloromethane solution and they attributed this to the formation of Co(IV) by the oxidation of the Co(III) complex with Br$_2$. Since it is highly unlikely that air oxidation can lead to the formation of Co(IV) from Co(II), the spectrum reported in our case is assigned to the O$_2$ adduct of the Co(II) complex. It is worth pointing out that this spectrum is similar (with nearly same parameters) to that of the Co(IV) species mentioned above, making it impossible to distinguish between the two, based on EPR spectra alone. The EPR spectrum of the bqdH$_2$ complex was much less resolved and deteriorates upon exposure of the sample to air (figure 3). Spectral simulations were unsatisfactory in this case.

The magnetic susceptibility of the pqdH$_2$ complex in the temperature range 20–295 K closely fits the Curie law with a low magnetic moment (0·9 B. M. based on Co(pqdH)$_2$). This is consistent with the formulation of the product as a mixture of paramagnetic and diamagnetic substances. While the obvious choice for the diamag-

netic component would have been the peroxo dimer, the elemental composition favours $Co(pqdH)_3$. It may be recalled that octahedral Co(III) complexes can be prepared from Co(II) salts and suitable ligands in presence of air (Greenwood and Earnshaw 1984). However, this is the first time that the dioxygen complex which could be an intermediate in the process is detected by EPR. The electronic spectrum of this compound in chloroform consists of a strong absorption in the visible region at 20·0 kK ($\varepsilon = 1\cdot0 \times 10^4 \, l \, mole^{-1} \, cm^{-1}$). In pyridine solution the band is shifted to 22·0 kK ($\varepsilon = 4\cdot4 \times 10^4 \, l \, mole^{-1} \, cm^{-1}$). The high values of the extinction coefficient imply that these bands correspond to charge transfer excitations rather than ligand field transitions.

Figure 4 shows the EPR spectrum of the doped sample $Co(pqdH)_2/Ni(pqdH)_2$ at 108 K. The spectrum is clearly identifiable as arising from a low spin cobalt(II) complex. There is an unidentified sharp signal in the host compound itself, seen also at room temperature, at nearly free electron g-value which overlaps with the Co(II) signals in the central part of the spectrum. No spectrum from $Co(pqdH)_2$ is obtained at room temperature. which is a consequence of fast relaxation via spin-orbit coupling to low-lying quartet states, as is usually the case with planar Co(II) complexes. The EPR parameters ($g_x = 2\cdot150$, $g_y = 2\cdot20$, $g_z = 2\cdot01$, $A_x = \cdot0028 \, cm^{-1}$, $A_y = 0\cdot0066 \, cm^{-1}$, $A_z = 0\cdot0141 \, cm^{-1}$) correspond to a $^2A_1(|z^2\rangle)$ ground state (McGarvey 1975; Daul *et al* 1979). Assuming that the ligand field parameters are not widely different in Schiff base
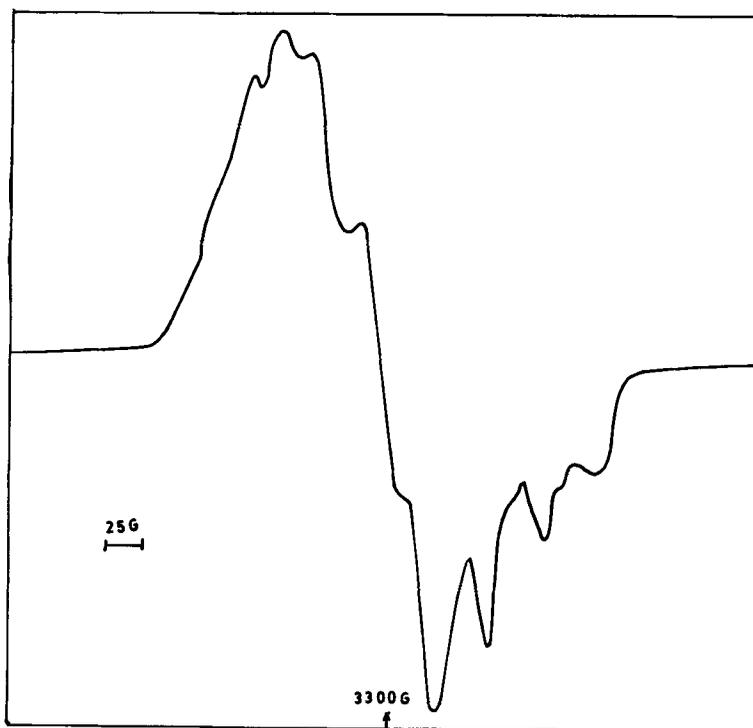

Figure 3. Polycrystalline EPR spectrum of the Co(II) complex of $bqdH_2$, at *X*-band and 298 K.
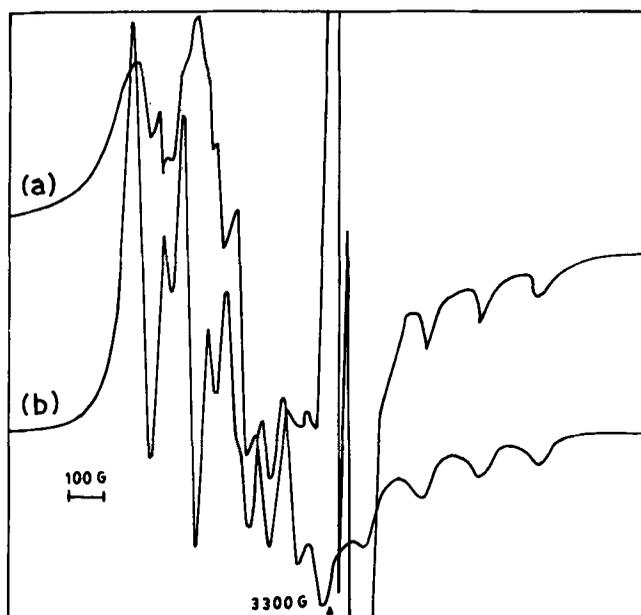
Figure 4. X-band EPR spectrum of the doped polycrystalline sample of $Co(pqdH_2)/Ni(pqdH_2)$ at 108 K: (a) experimental spectrum; (b) simulated spectrum. The intense signals in the centre of the spectrum are due to an unidentified radical present in the host compound itself.

and oxime complexes, we find from published plots (Daul *et al* 1979) that the $^2A_1$ ($|z^2\rangle$) state is about $5000\,cm^{-1}$ below the $^2A_2(|yz\rangle)$ state. In the case of Schiff base complexes the $|z^2\rangle$ ground state is observed mainly in coordinating solvents but not in Ni(II) host compounds (Daul *et al* 1979). In free Co(salen), two magnetically dilute sites are observed in oxygenated samples (Murray *et al* 1986). One site belongs to $|z^2\rangle$ ground state thought to arise from axial perturbation by oxygen atoms of the neighbouring molecules, while the second site which is observed only after repeated oxygenation/ deoxygenation cycles belongs to the $|yz\rangle$ state and is ascribed to planar four-coordinate Co(salen) molecules {salen = N,N'-ethylene*bis*(salicyladimine)}. The adoption of $|z^2\rangle$ ground state by the present dioximato complex in the nickel host complex implies that the separation between $^2A_1(|z^2\rangle)$ and $^2A_2(|yz\rangle)$ states is small in the isolated planar complex (believed to have $^2A_2$ ground state), so that weak axial perturbation by the host lattice is sufficient to cause a switch over to the $^2A_1$ state. This is consistent with the greater reactivity towards oxygen leading to eventual oxidation of the metal centre.

Acknowledgement

References

Basset R C J, Denney R C, Jeffery G H and Mendham J (eds) 1982 *Vogel's textbook of quantitative inorganic analysis* (London:ELBS and Longman) pp. 461
Baumgarten M, Lubitz W and Winscom C J 1987 *Chem. Phys. Lett.* **133** 102
Biskupic S and Valko L 1975 *J. Mol. Struct.* **27** 97
Boyer J H and Ellzey S E Jr 1960 *J. Am. Chem. Soc.* **82** 2525
Chacko V P and Manoharan P T 1974 *J. Magn. Reson.* **16** 75
Daul C, Schlapfer C W and Zelewsky A V 1979 *Struct. Bonding* **36** 129
Greenwood N N and Earnshaw A 1984 *Chemistry of the elements* (Oxford: Pergamon) p. 1302
Gupta B D, Kumar M and Roy S 1989 *Inorg. Chem.* **28** 11
Herron N 1986 *Inorg. Chem.* **25** 4714
Hitchman M A 1977 *Inorg. Chem.* **16** 1985
Jones R D, Summerville D A and Basolo F 1979 *Chem. Rev.* **79** 139
Jorin E, Schweiger A and Gunthard Hs H 1979 *Chem. Phys. Lett.* **61** 228
Kamachi M, Shibasaka M, Kajiwara A, Mori W and Kishita M 1989 *Bull. Chem. Soc. Jpn.* **62** 2465
Kanzing W and Cohen M H 1959 *Phys. Rev. Lett.* **3** 509
Lopez C, Alverez S, Solans X and Font-Altaba M 1986 *Inorg. Chim. Acta* **111** L19
Lubitz W, Winscom C J, Diegruber H and Moseler R 1987 (unpublished results) (quoted in Baumgarten *et al* 1987)
McGarvey B R 1975 *Can. J. Chem.* **53** 2498
Murray K S, van den Bergen A, Kennedy B J and West B O 1986 *Aust. J. Chem.* **39** 1479
Rajasekharan M V and Manoharan P T 1981 *Mol. Phys.* **44** 1145
Rockenbauer A, Zahonyi E D and Simandi L I 1975 *J. Chem. Soc., Dalton Trans.* 1729
Schmidt J and Soll J 1907 *Berichte* **40** 2456
Smith T D and Pilbrow J R 1981 *Coord. Chem. Rev.* **39** 295.
Swarnabala G and Rajasekharan M V 1989 *Inorg. Chem.* **28** 662
Walter C 1936 *Gazz. Chim. Ital.* **66** 595