

- J. Biol. Chem.*, **251**, 801 (1976).
 (3) T-W. Wu, *Israel J. Chem.*, **23**, 241 (1983).
 (4) C. Jacobsen, *Eur. J. Biochem.*, **27**, 513 (1972).
 (5) J. Jacobsen, *Int. J. Peptide Protein Res.*, **9**, 235 (1977).
 (6) J. M. Van der Eijk, R. J. M. Nolte, V. E. M. Richterw, and W. Dren th, *Biopolymers*, **19**, 445 (1980).
 (7) T. G. Waddell, D. E. Leyden, and M. T. DeBello, *J. Amer. Chem. Soc.*, **103**, 5303 (1981).
 (8) A. F. McDonagh and L. A. Palma, *Biochem. J.*, **189**, 193 (1980).
 (9) D. A. Lightner adn Y-T. Park, *Tetrahedron* **35**, 463 (1979).

The Oxidation of Hydrazobenzene by Oxygen Catalysed by Co(3MeOsalen) in Methanol

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The oxidation of hydrazobenzene by oxygen in methanol solution is catalysed by Co(3MeOsalen) which is a synthetic oxygen carrier. The products are *trans*-azobenzene and water. The rate of the reaction has been studied spectrophotometrically and the rate law established. A mechanism involving a ternary complex of catalyst, hydrazobenzene and oxygen has been proposed.

1. Introduction

It has been known since the observations of Pfeiffer and his co-workers in 1933¹ that cobalt(II) Schiff's base complexes *e.g.* Co(salen), Figure 1, form reversible complexes with oxygen. There has been considerable recent interest in these compounds because of their relationship to the natural iron-containing oxygen carriers hemoglobin and myoglobin.² Hemoglobin and myoglobin consist of an iron-porphyrin complex, the haem group, embedded in the protein which provides one axial ligand, an imidazole group, to the iron. On oxygenation the sixth coordination site of the iron accepts the dioxygen ligand. Thus the ligand field about the iron in oxyhemoglobin is approximately octahedral.³

Cobalt(II) Schiff's base complexes are square planar with a low spin d^7 electron configuration. The binding of an axial, fifth ligand leads to a ground state with the unpaired electron in the d_z^2 orbital. This electron configuration is a necessary prerequisite for the binding of dioxygen.⁴ Drago and Corden⁵, in their spin-pairing model for the binding of dioxygen, presented evidence

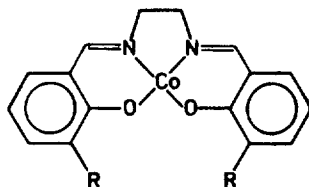


Figure 1. Structure of Schiff-base complexes. R = H, Co(salen); R = CH₃O, Co(3MeOsalen).

that the odd electron in the oxygenated complex is in the dioxygen π^* orbital, but that the extent of electron transfer from cobalt to oxygen is dependent on the nature of the equatorial and axial ligands. In the extreme case of complete electron transfer the complex could be formulated as cobalt(III)-superoxide. The change in the electronic structure of oxygen from the relatively unreactive triplet ground state to a doublet coordinated species, with a weakened O-O bond bearing fractional negative charge, could be expected to enhance the reactivity of oxygen in radical or nucleophilic reactions.

Cobalt(II) Schiff's base complexes with added axial ligands have been shown to catalyse the oxidation by oxygen of secondary alcohols⁶ to ketones, and of phenols⁷ to quinones. The structurally related bis(dimethylglyoximate) cobalt(II) has been reported to catalyse the oxidation of hydrazobenzene to azobenzene in the presence of triphenylphosphine.⁸ Kinetic studies^{6,7} have shown that in the oxidation of alcohols and phenols the transition state is a ternary complex of dioxygen, cobalt catalyst (including axial base) and substrate. Thus the reactions resemble an enzyme-catalysed process in which the two substrates, dioxygen and the organic molecule, are brought together by the catalyst. In this paper we show that the oxidation of hydrazobenzene catalysed by Co(3MeOsalen), Figure 1, follows a similar kinetic scheme, providing evidence of saturation of the catalyst by the substrate as an enzyme catalysed reaction.

Autoxidation of hydrazobenzene was first described in 1901 by Manchot and Herzog.⁹ This, and later work^{10,11} has shown

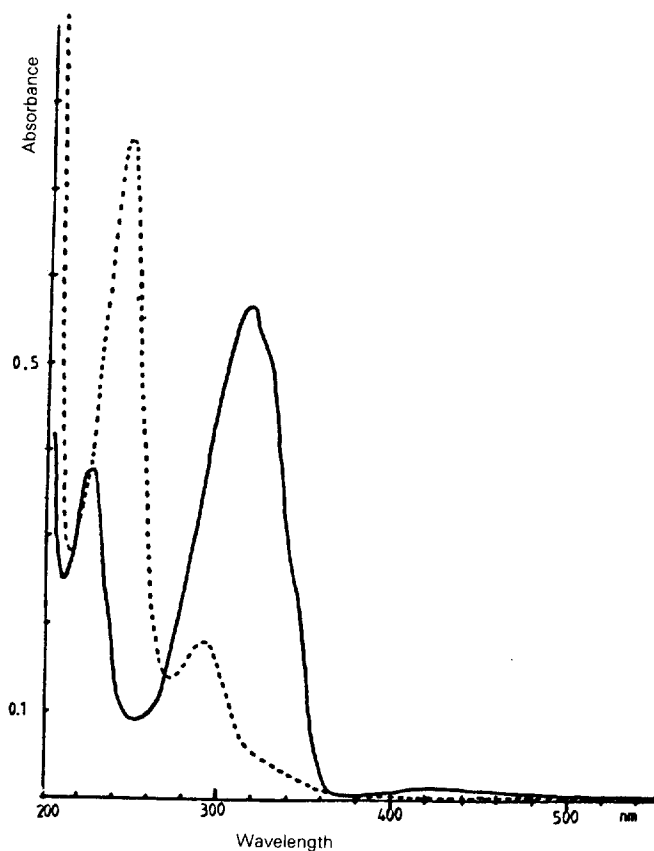


Figure 2. Absorption spectra of hydrazobenzene (broken curve, concentration $3.45 \times 10^{-5}M$) and *trans*-azobenzene (solid curve, $2.75 \times 10^{-5}M$). Methanol, 25 °C.

TABLE 1: Absorption maxima of species used in this work*

Hydrazobenzene H ₂ AB		<i>trans</i> -Azobenzene AB		<i>cis</i> -Azobenzene ^b	
λ_{\max} nm	ϵ $10^3 M^{-1}cm$	λ_m nm	ϵ $10^3 M^{-1}cm^{-1}$	λ_{\max} nm	ϵ $10^3 M^{-1}cm^{-1}$
245	21.81	315	16.1	281	4.99
289	5.23	437	0.5	433	1.48

* 25 °C, methanol; ^b 25°C, methanol; ^c Ethanol, Ref. 15.

that the products are *trans*-azobenzene and hydrogen peroxide with the reaction first order in hydrazobenzene and oxygen.

Results and Discussion

Absorption spectra of hydrazobenzene (H₂AB) and *trans*-azobenzene (AB) are shown in Figure 2. Extinction coefficients for these and of *cis*-azobenzene are given in Table 1. The spectral changes during the reaction are indicated in Figure 3. The band at 254 nm due to the oxidation of H₂AB decreases with time in Figure 3-b, while bands at 315 nm and 440 nm (see Figure 2), attributable to *trans*-azobenzene in Figure 3-a,b increase. There is an isosbestic point at 280 nm, and in particular there is no new band at 281 nm. Hence the reaction product is *trans*-azobenzene, with negligible production of *cis* isomer.

Kinetic measurements were made at 315 nm. A typical curve of absorbance *A* versus time *t* is shown in Figure 4. Plots of $\log(A_{\infty} - A)$ against *t* were found to be curved after approximately one half-life indicating deviation from pseudo-first order kinetics. Figure 4 includes a pseudo-first order curve calculated

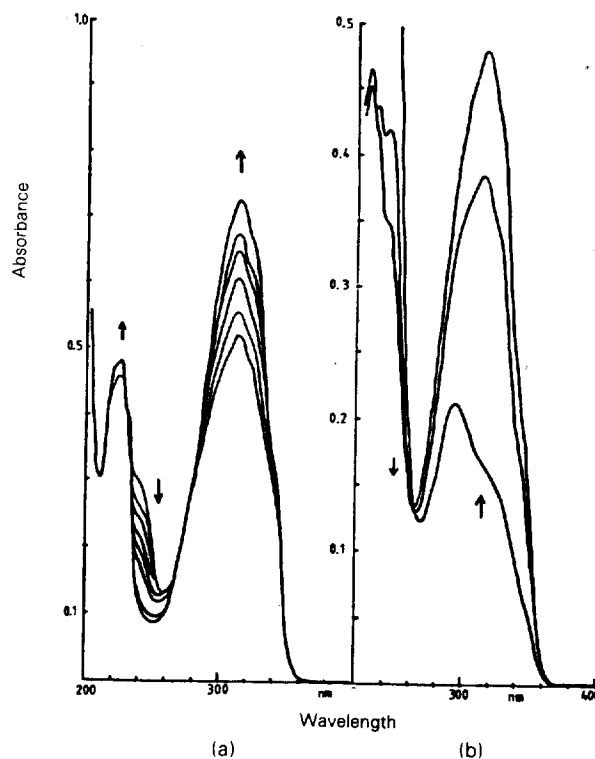


Figure 3. Changes in absorption spectra during reaction. $[H_2AB]_0 = 3.33 \times 10^{-3}M$, $[Co]_r = 5.2 \times 10^{-6}M$. O₂ saturated in methanol, 1 atm., 25 °C.

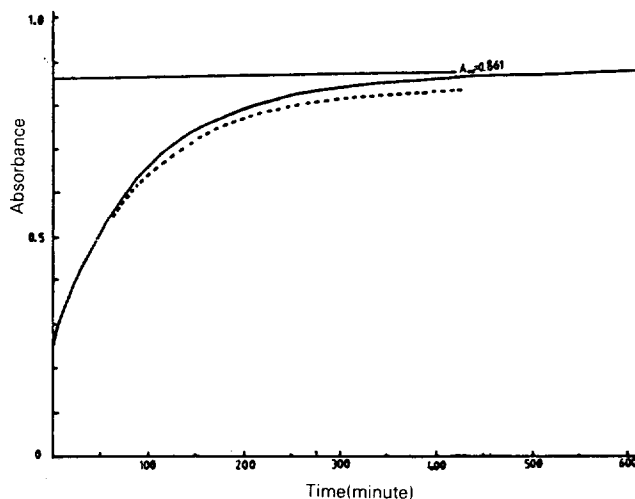


Figure 4. Plot of absorbance *A* (at 315nm) against time. $[H_2AB]_0 = 3.26 \times 10^{-5}M$, $[Co]_r = 5.67 \times 10^{-6}M$. O₂ saturated methanol, 1 atm, 25 °C. Solid curve, experimental; broken curve, calculated for pseudo-first order kinetics as described in the text.

to fit the earlier part of the data, and comparison with the experimental data shows that the experimental rate increased over that defined by the rate constant. The deviations may be due to some side reaction involving the hydrogen peroxide which is formed in the reaction.

To avoid this complication, initial rates R_0 were calculated from slopes of tangents at $t=0$:

$$R_0 = l^{-1} (\Delta \epsilon)^{-1} (dA/dt)_0 \quad (1)$$

which is derived from $A = \epsilon l$ where *l* is the path length and $\Delta \epsilon = 25.5 M^{-1}cm^{-1}$ obtained from intercept with $\log R_0$ against $\log (dA/dt)_0$. The dependence of rate on total cobalt concen-

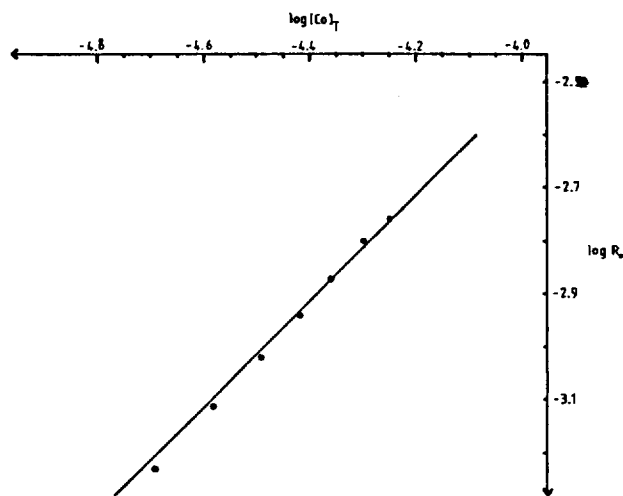


Figure 5. Plot of $\log R_0$ against $\log [Co]_T$. $[H_2AB]_0 = 4.11 \times 10^{-4} M$. $[Co]_T = 7.27 \times 10^{-6} M$; curve (b) air saturated, $[Co] = 7.43 \times 10^{-6} M$.

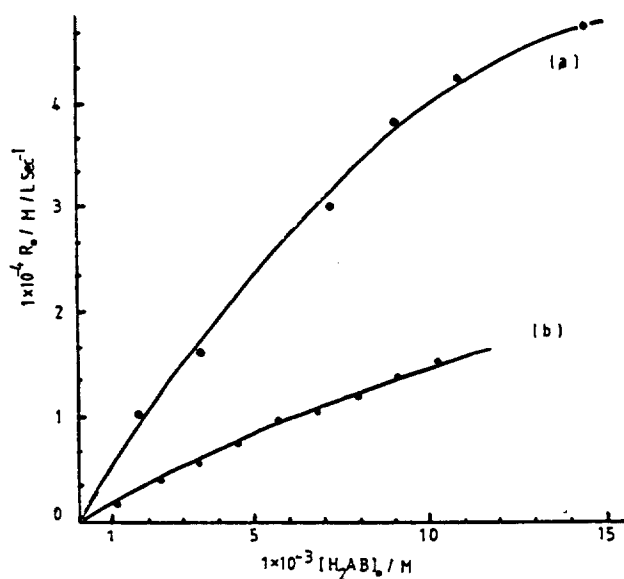


Figure 6. Plots of initial rate R_0 against $[H_2AB]_0$. Curve (a) O_2 saturated, $[Co]_T = 7.27 \times 10^{-6} M$; curve (b) air saturated, $[Co] = 7.43 \times 10^{-6} M$, Methanol, $25^\circ C$.

tration $[Co]_T$ is linear, over the range $[Co]_T = (1.5-5.6) \times 10^{-6} M$, Figure 5. The hydrazobenzene dependence is non-linear, suggesting an equilibrium saturation effect, Figure 6. The oxygen dependence, based on measurements at two concentrations, is also non-linear as discussed below.

Discussion

The data suggest the formation of a ternary complex $CoL.H_2AB.O_2$ (where $L = 3MeOsalen$). For completeness, we introduce stepwise equilibria for the formation of this complex, via the two binary complexes $CoL.H_2AB$ and $CoL.O_2$:

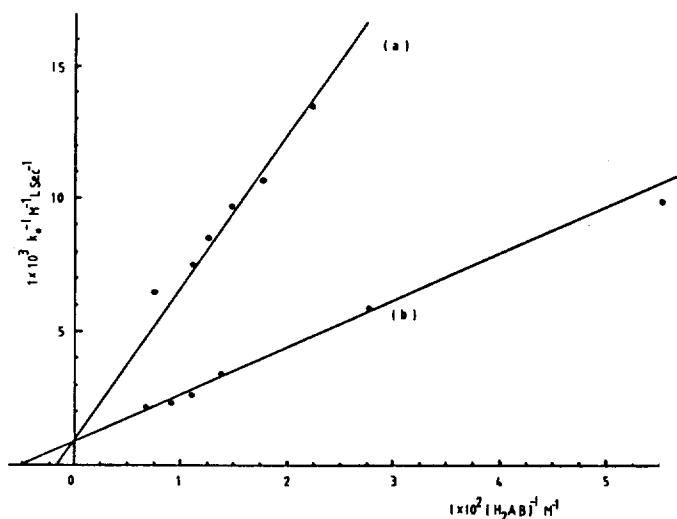
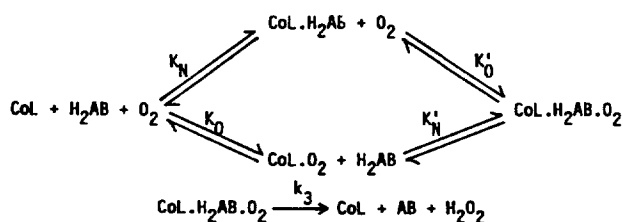


Figure 7. Plots of k_0^{-1} against $[H_2AB]_0^{-1}$. Curve (a) air saturated; curve (b) oxygen-saturated; 1 atm, methanol, $[Co]_T = 7.3 \times 10^{-6} M$, $25^\circ C$.

TABLE 2: Rate and Equilibrium Constants at $25^\circ C$

K_N	$0 \pm 10 M^{-1}$
k_3	$77 \pm 5 s^{-1}$
$\frac{1 + K_0 [O_2]}{k_3 K [O_2]}$	$4.33 \times 10^{-4} Ms ([O_2] = 1.96 \times 10^{-3} M)$
	$1.29 \times 10^{-4} Ms ([O_2] = 9.63 \times 10^{-3} M)$
K_0	$70 \pm 7 m^{-1}$
K	$(8.7 \pm 0.8) \times 10^3 M^{-2}$

Under the experimental conditions $[O_2] > [H_2AB] > [CoL_2]$ the rate of reaction is given by

$$R = \frac{d[AB]}{dt} = \frac{k_3 K [Co]_T [H_2AB] [O_2]}{1 + K_N [H_2AB] + K_0 [O_2] + K [H_2AB] [O_2]} \quad (4)$$

which may be expressed as

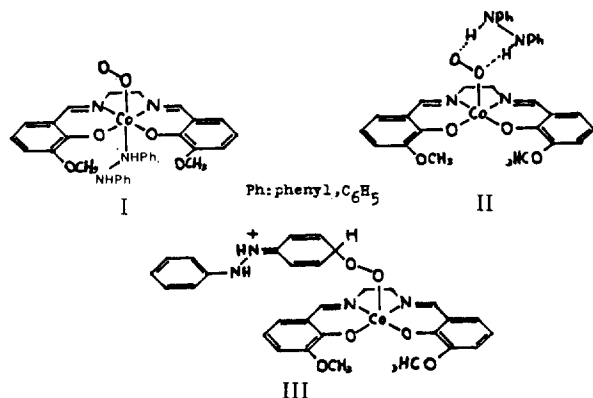
$$\frac{1}{k_0} = \frac{1}{k_3} \left(1 + \frac{K_0}{K [H_2AB]_0} + \frac{K_N}{K [O_2]} + \frac{1}{K [H_2AB]_0 [O_2]} \right) \quad (5)$$

where $k_0 = R_0/[Co]_T$, $K = K'_O K_N = K_0 K'_N$, and $[H_2AB]_0$ is the initial hydrazobenzene concentration. Thus it is expected that plots of k_0^{-1} against $[H_2AB]_0^{-1}$ at constant $[O_2]$ will be linear. The slopes of such plots are $(1 + K_0 [O_2])$, and it is noteworthy that the plots for different O_2 concentrations should intersect in a single point, with $[H_2AB]_0^{-1} = -K_N$, and $k_0^{-1} = k_3^{-1} (1 - K_0 K_N / K)$.

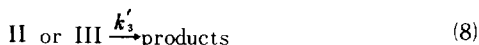
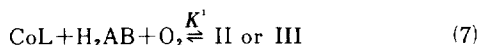
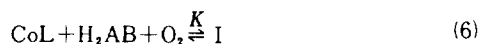
As shown in Figure 7, the plots K_0^{-1} against $[H_2AB]_0^{-1}$ are in fact linear, and the intersection point lies on the vertical axis, within experimental error. The reaction via the complex $CoL.H_2AB$ does not occur, and thus $K_N = 0$, and the value of k_3 may be read directly from the intersection point, while the slopes of the two lines give K_0 and K . Value of these constants, with estimated limits of error, are shown in Table 2.

A possible structure for the ternary complex is I below. However, this is not necessarily the effective reaction intermediate. To account for the hydrogen abstraction, an alternative structure II (the vacant site on Co may be occupied by CH_3OH) with N-H-O bridging might seem attractive, analogous to that suggested by Savitskii⁶ for alcohol oxidation. However, in a concerted reaction this would be expected to lead to *cis*-azobenzene, which was not observed. The isomerisation

of *cis*-azobenzene to the *trans* isomer was considerably slower than the oxidation of hydrazobenzene, and was not catalysed by Co(3MeOsalen). An intermediate III in which the dioxygen has attacked *para* to the azo-group, as suggested for the autoxidation reaction¹¹ and the cobalt catalysed oxidation of phenols,⁷ would lead to the more stable *trans* isomer, and must also be considered. Further work is required to characterise the intermediates.



The reaction pathway may be written



where the two equilibria are rapid and $K'k_3' = Kk_3$

The situation in which an association complex is detected, but some other species of the same composition, but relatively less stable, is the true reaction intermediate, is paralleled in many other reactions *e.g.* electron transfer by the 'dead-end' mechanism.¹² The stability constants K_N , K_0 , K , however, still relate to the predominant complex I, and it is of interest that K_N is much smaller than K_N' . The upper limit of K_N is estimated as 10 M^{-1} while $K_N' = K/K_0 = 124 \text{ M}^{-1}$. The difference can be understood if the d_{z^2} electron in complex I is partially delocalised onto the O_2 molecule⁵, so that the effective oxidation state of cobalt is intermediate between Co^{II} and Co^{III} .

Experimental

$\text{H}_2(3\text{MeOsalen})$ was prepared by the method of Diehl *et al*¹³. 3-methoxysalicylaldehyde (35.5 mmoles) was dissolved in hot absolute ethanol (25 ml) and the solution stirred for 30 minutes ethanol. Yield 72 % mp 162–163°C, as reported. Elemental analysis based on $\text{C}_{18}\text{H}_{20}\text{N}_2\text{O}_4$: calculated C: 65.9, N: 8.5, H: 6.1; found: C: 65.6, N: 8.4, H: 6.2

The catalyst Co^{II} (3MeOsalen), was prepared by the method of Diehl *et al*¹³, as modified by Beckett¹⁴. The ligand, $\text{H}_2(3\text{MeOsalen})$ (35.5 mmoles) was dissolved in absolute ethanol (300 ml) and cobalt (II) acetate tetrahydrate (35.5 mmoles) was dissolved in hot water under nitrogen and added dropwise to the solution of the ligand. The pink solution changed to dark

red. After cooling, a silver gold precipitate was formed. The product was filtered, washed with ethanol (30 ml) and then water (30 ml), and finally dried in vacuo at 180 °C for at least two hours. The colour of the product changed from silver gold to violet. Yield 52%. Elemental analysis based on $\text{CoO}_4\text{N}_2\text{C}_{18}\text{H}_{18}\text{O}_2$: calculated: C: 51.80, H: 4.36, N: 6.71; found: C: 52.15, H: 4.74, N: 6.87.

Hydrazobenzene (Aldrich) was always kept in a dry nitrogen glove bag. Dry nitrogen was produced by passing cylinder nitrogen over P_2O_5 . Oxygen saturated reaction mixtures were made by bubbling oxygen through the solution for fifteen minutes.

The rates of the reactions were followed by observing absorbance changes against time in the reaction mixtures at a wavelength of 325 nm or 437 nm in 1 cm cells. The reactions were conducted at a tenfold molar excess or more of hydrazobenzene over the cobalt(II) complex. The absorption spectra were measured on a Pye Unicam SP8-200 spectrophotometer.

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References

- (1) P. Pfeiffer, E. Breith, E. Lubbe, and T. Tsumaki, *Justus Liebigs Ann.Chem.*, **503**, 84 (1933).
- (2) R. D. Jones, D. A. Summerville and F. Basolo, *Chem. Rev.*, **79**, 139 (1979).
- (3) M. F., Perutz, *Brit. Med. Bull.*, **32**, 195 (1976).
- (4) T. D. Smith and J. R. Pilbrow, *Coord. Chem. Rev.*, **39**, 295 (1981).
- (5) R.S. Drago and B.B., Corden, *Acc. Chem. Res.*, **13**, 353 (1980).
- (6) A. V. Savitskii, *J. Gen. Chem. USSR*, **44**, 1518 (1974).
- (7) A., Zombeck, R. S. Drago, B. B. Corden, and J. H. Gaul, *J. Amer. Chem. Soc.*, **103**, 7580 (1981).
- (8) S., Nemeth, Z. Szeverenyi and L.I. Simandi, *Inorg. Chim. Acta*, **44**, L107 (1980).
- (9) W. Manchot and J. Herzog, *Justus Liebigs Ann.Chem.*, **316**, 331 (1901).
- (10) J. H. Walton, G. W. Filson, *J. Amer. Chem. Soc.*, **54**, 3228 (1932).
- (11) G. Kaupp and G. A. Russell, *Chem. Ber.*, **101**, 1729 (1968).
- (12) L. Rosenhein, D. Speiser, and A. Haim, *Inorg. Chem.*, **13**, 1571, (1974).
- (13) H. Diehl, L. M. Liggett, C. C. Hach, G.C. Harrison, L. Henselmeier, R. W. Schwant and J. Mathews Jr., *Iowa State Coll. Jour. Science*, **22**, 110 (1947).
- (14) M. A. Beckett, Ph.D. Thesis, University of East Anglia, (1981).
- (15) F., Gerson, E., Heilbronner, A. van Veen and B. M. Wepster, *Helv. Chim. Acta*, **43**, 1889 (1960).