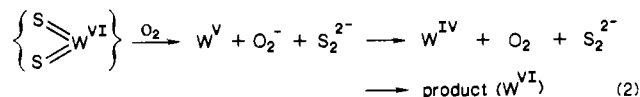


gains maximum intensity after 8 h, starts decaying, and disappears after 20 h. The observed reaction does not take place if it is carried out in an inert atmosphere, eliminating  $H^+$  as an alternative electron acceptor.<sup>11</sup> The disappearance of the EPR active species after 20 h might be due to (i) dimerization of EPR-active W(V), (ii) oxidation of W(V) to W(VI), or (iii) further reduction of W(V) to W(IV). Possibility i seems likely as no dimeric W(V) compound could be isolated under the reaction conditions within 40 h.<sup>12</sup> For possibility ii the oxidation of W(V) to W(VI) should lead to the formation of the product immediately after the disappearance of EPR signal (20 h after the reaction is started). However, workup at this stage gives the product,  $[WO(S_2)(S_2CNEt_2)_2]$ , in low yield (~30%).<sup>13</sup> Thus to increase the formation of the product to 70% (final yield), the last 16 h, when the solution is EPR silent, is essential (total reaction time 36 h). This gives indirect support to possibility iii and suggests that electron transfer from the  $S^{2-}$  ligand to W(VI) takes place to produce W(IV) via a kinetically competent W(V) species. Proof for the acceptance of one electron by oxygen to generate  $O_2^-$  in situ is furnished by observing an EPR signal due to  $O_2^-$ <sup>14</sup> ( $g_{\parallel} = 2.14$ ,  $g_{\perp} = 2.00$ ) (Figure 1). In addition an EPR signal due to  $S_3^-$  ( $g = 2.028$ ) is also seen.<sup>15,16</sup> Thus, internal and external oxidants share one electron each donated by two  $S^{2-}$  ligands with the formation of one  $S_2^{2-}$ .

When the W(V) EPR signal was at a maximum (after 8 h) an aliquot of the reaction mixture was treated with an excess of solid  $KO_2$  and then subjected to EPR measurements at room temperature. The W(V) EPR signal disappeared after 4 h compared to 12 h for the  $KO_2$ -untreated aliquot. The disappearance of the W(V) EPR signal more quickly in the presence of  $KO_2$  than in its absence is consistent with the reduction of W(V) to W(IV) by  $O_2^-$ , which is a moderate reducing agent in aprotic media.<sup>17</sup> Recently, the reduction of Mo(V) to Mo(IV) by  $O_2^-$  has also been reported.<sup>18</sup> Attempts to isolate the intermediate W(V) species as a solid failed. However, under identical reaction conditions, the corresponding dimethylammonium salt of  $WOS_3^{2-}$  gave a brown product that shows an EPR signal characteristic of W(V) ( $g = 1.879$ ). This compound  $[WO(S_2CNMe_2)_3]$ <sup>19</sup> in  $CH_2Cl_2$  solution containing 5% v/v DMSO reacts slowly with  $K^+O_2^-$  to give  $[W^{IV}O(S_2CNMe_2)_2]$ .<sup>20</sup>

The concentration of W(V) at 8 h reaction time was estimated to be 22% of the total tungsten by weighing a cutout absorption curve. The concentration of W(V) remains more than 10% between the 5th and the 13th hour of the total reaction period of 36 h. Stability of the W(V) species for hours under the experimental conditions is not expected. This can be explained by the generation of W(V) species from W(VI) followed by further reactions between W(V),  $O_2^-$ , and/or several other species that are generated as side products.<sup>16</sup> However, the long time stability of W(V) species establishes a kinetically competent reaction for its generation over the other side reactions.

Thus, we suggest that the main electron-transfer pathway can be described as in (2).



The last step of oxidation of W(IV) to the product is achieved by aerial oxygen in the presence of polysulfide, which is a by-product of the reaction.<sup>20</sup> The entire process of this ligand to metal electron flow is controlled by the external oxidant, oxygen, functioning as an electron acceptor. The role of tungsten is to function as an electron sink, which is very similar to the role of molybdenum in the substrate reduction phase of xanthine oxidase turnover.<sup>21</sup>

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**Registry No.**  $(Et_2NH)_2WOS_3$ , 112296-52-3;  $[WO(S_2)(S_2CNEt_2)_2]$ , 108556-13-4;  $CS_2$ , 75-15-0;  $O_2$ , 7782-44-7.

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Department of Chemistry  
Indian Institute of Technology  
Kanpur 208016, India

Mohammad A. Ansari  
Jayanthi Chandrasekaran  
Sabyasachi Sarkar\*

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- (11) (a) The reaction does not take place in  $H_2S$  atmosphere. (b) As suggested by one of the reviewers, incubation of the reaction mixture under an inert atmosphere ( $N_2$ ) for 20 h followed by exposing the mixture to air takes a further 36 h to complete the reaction. This eliminates direct anaerobic reduction of W(VI) to W(IV) under the reaction conditions with the oxidation of W(IV) by aerial oxygen to W(V) as a side reaction.
- (12) Thermal reaction of the product or keeping it for weeks in solution gives the W(V) dimer,  $[W_2O_2(\mu-S_2)(S_2CNEt_2)_2]$ : Ansari, M. A.; Chandrasekaran, J.; Sarkar, S. *Bull. Chem. Soc. Jpn.* in press.
- (13) Workup of the reaction mixture at this stage gives mostly the unreacted starting material.
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- (16) (a) The formation of  $S_3^-$  suggests the involvement of many side reactions associated with the main reaction. It is well-known that aerial oxygen oxidizes sulfide to elemental sulfur especially in the presence of transition-metal ions. Furthermore,  $S_2^{2-}$  reacts with elemental sulfur to produce higher polysulfides, which in polar solvents like DMF may dissociate to generate radicals like  $S_3^-$ . This process may be more complicated in the presence of W(V) and  $O_2^-$ . (b) We have checked the reaction of elemental sulfur in the presence of  $KO_2$  in DMF by EPR, which shows the formation of  $S_3^-$ .
- (17) Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*, 4th ed.; Wiley: New York, Chichester, Brisbane, Toronto, 1980; pp 490-491.
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- (19) The compound has been tentatively identified as  $[WO(S_2CNMe_2)_3]$  on the basis of elemental analysis and IR and EPR spectroscopy.
- (20)  $[W^{VI}O(S_2)(S_2CNEt_2)_2]$  on reacting with  $CN^-$  produces  $[W^{IV}O(S_2CNEt_2)_2]$ , which is more stable than its molybdenum analogue. This compound on prolonged stirring with polysulfide or elemental sulfur reverts back to  $[W^{VI}O(S_2)(S_2CNEt_2)_2]$  (see ref 7c,d). The possibility that the last step in the mechanism of reaction 1 involves an oxidation, parallel to this type of reaction, is not excluded.

## Cobalt(III) Complexes of

### 1,3-Propanediamine-*N,N'*-diacetic-

### *N,N'*-di-3-propionic Acid and

### 1,3-Propanediamine-*N-3-propionic-N,N',N'*-triacetic Acid

Sir:

For (diamine-*N,N'*-diacetato-*N,N'*-di-3-propionato)metal(III) complexes, three geometrical isomers, differing in the number (2, 1, or 0) of six-membered carboxylate rings lying in the G plane, are possible: trans( $O_5$ ) (I), trans( $O_5O_6$ ) (II), and trans( $O_6$ ) (III) (Figure 1a). On the other hand, the unsymmetrical ligand 1,3-propanediamine-*N-3-propionate-N,N',N'*-triacetate (1,3-pdp3a) can form only two geometrical isomers upon coordination, trans( $O_5$ ) (I) and trans( $O_5O_6$ ) (II) (Figure 1b).

We report the synthesis of the ligand 1,3-propanediamine-*N,N'*-diacetate-*N,N'*-di-3-propionate (1,3-pddadp) in good yield along with small amounts of 1,3-pdp3a and the earlier reported<sup>1,2</sup> 1,3-propanediaminetetraacetic acid ( $H_4pdta$ ). Two isomers of  $[Co(1,3-pddadp)]^-$  and one of  $[Co(1,3-pdp3a)]^-$  were isolated and

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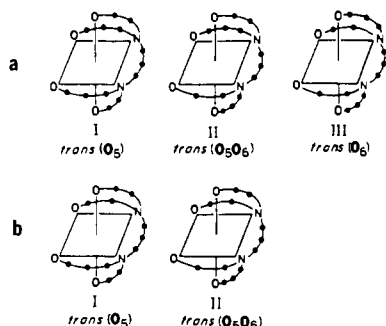


Figure 1. Possible geometrical isomers of (a)  $[\text{Co}(1,3\text{-pddadp})]^-$  and (b)  $[\text{Co}(1,3\text{-pdp3a})]^-$ .

the geometrical isomers identified on the basis of absorption and NMR spectra.

For  $[\text{M}(\text{edta-type})]^-$  complexes<sup>3-5</sup> the glycinate rings lying in the plane of the diamine ring (G rings) are more strained than the out-of-plane rings (R rings). Because of the strain of G rings, the ethylenediamine- $N,N'$ -diacetate- $N,N'$ -di-3-propionate (eddadp) ligand preferentially forms isomers having six-membered (3-propionate) rings in equatorial positions. Two isomers ( $\text{trans}(\text{O}_5)$  (I) and  $\text{trans}(\text{O}_5\text{O}_6)$  (II) of the  $[\text{Co}(\text{eddadp})]^-$ <sup>6</sup> and  $[\text{Rh}(\text{eddadp})]^-$ <sup>7</sup> complexes have been prepared and characterized. In the case of the corresponding Cr(III) complex<sup>5,8</sup> only the favored  $\text{trans}(\text{O}_5)$  isomer has been isolated.

The 1,3-pddadp ligand, with a three-carbon diamine "backbone" ring, can be expected to form all possible geometrical isomers, as reported for the  $[\text{Cr}(1,3\text{-pddadp})]^-$  complex.<sup>9</sup> The Cr(III) complexes were prepared by using the condensation mixture from the ligand synthesis, without isolation.

1,3-Propanediamine- $N,N'$ -diacetic- $N,N'$ -di-3-propionic acid was prepared by condensation of 1,3-propanediamine- $N,N'$ -diacetic acid with 3-chloropropionic acid in aqueous KOH solution. The acid was precipitated as the white barium salt  $\text{Ba}_2(1,3\text{-pddadp})\cdot 8\text{H}_2\text{O}$  (yield 53.4%). The Ba salt was reconverted to the acid by precipitation of  $\text{BaSO}_4$  with  $\text{H}_2\text{SO}_4$ . The acid crystallized from water-ethanol solution and was recrystallized from water-ethanol (1:3). Analytical data are given in Table I (supplementary material).

Two isomers of the cobalt(III) complex of 1,3-pddadp were prepared from  $\text{Co}(\text{OH})_3$  (0.02 mol) and an aqueous solution of the ligand (0.02 mol) containing 0.02 mol of KOH. These isomers were separated by passing the resulting solution of the complex through an ion-exchange column to give two bands. The eluates of these bands were desalted by using a G-10 Sephadex column. Yield:  $\text{trans}(\text{O}_5\text{O}_6)$  isomer (first eluate), 1.5 g;  $\text{trans}(\text{O}_6)$  isomer (second eluate), 3.5 g.

The condensation mixture (without isolation of  $\text{H}_4\text{-1,3-pddadp}$ ) was used directly to prepare cobalt(III) complexes, yielding four bands by ion-exchange chromatography. The first two bands yielded the two isomers of  $[\text{Co}(1,3\text{-pddadp})]$  isolated above. The third band was the hexadentate complex  $[\text{Co}(1,3\text{-pdp3a})]\cdot 2\text{H}_2\text{O}$ , and the fourth band was the earlier reported<sup>1</sup>  $[\text{Co}(1,3\text{-pdta})]$ . These were characterized by elemental analysis and NMR and absorption spectra.

Proton NMR spectra of these complexes were interpreted in light of the results obtained for multidentate (amino polycarboxylato)cobalt(III) complexes containing the various types of glycinate rings.<sup>10-12</sup> The  $^1\text{H}$  NMR spectrum of the  $\text{trans}(\text{O}_6)\text{-}[\text{Co}(1,3\text{-pddadp})]^-$  complex is very simple. In the glycinate region there is only one well-resolved AB pattern centered at 3.73 ppm with  $\delta_A$  4.11,  $\delta_B$  3.33, and  $J_{AB} = 16.6$  Hz. The results are in good agreement with the  $\text{trans}(\text{O}_6)$  isomer ( $C_2$  symmetry) having two equivalent glycinate G rings and two equivalent 3-propionate rings in axial positions. In the same spectral region, the  $\text{trans}(\text{O}_5\text{O}_6)\text{-}[\text{Co}(1,3\text{-pddadp})]^-$  complex ( $C_1$  symmetry) shows signals of glycinate methylenes for two well-resolved AB patterns ( $J_{AB} = 16.7$  Hz and  $J_{AB} = 18.8$  Hz) associated with an in-plane (G) ring (AB pattern centered at 3.57 ppm,  $\delta_A$  3.89,  $\delta_B$  3.24) and an out-of-plane (R) ring (AB pattern centered at 3.77 ppm,  $\delta_A$  3.82,  $\delta_B$  3.72).

Both isomers of the  $[\text{Co}(1,3\text{-pdp3a})]^-$  complex (Figure 1b) have the same  $C_1$  molecular symmetry. The  $^1\text{H}$  NMR spectrum of the one isomer isolated, in the expected region, reveals three resolved AB patterns, two nonequivalent G rings with  $J_{AB} = 15.7$  Hz (AB pattern centered at 3.83 ppm,  $\delta_A$  4.09,  $\delta_B$  3.57) and  $J_{AB} = 16.7$  Hz (AB pattern centered at 3.64 ppm,  $\delta_A$  3.90,  $\delta_B$  3.37) and one R ring with  $J_{AB} = 18.8$  Hz (AB pattern centered at 3.84 ppm,  $\delta_A$  4.11,  $\delta_B$  3.57). This suggests that it is the  $\text{trans}(\text{O}_5\text{O}_6)\text{-}[\text{Co}(1,3\text{-pdp3a})]^-$  isomer. This is unexpected since only one isomer was isolated and it might be expected to be the  $\text{trans}(\text{O}_5)$  isomer with the one propionate ring in the G plane to minimize strain.

The absorption spectra of  $[\text{Co}(1,3\text{-pdp3a})]^-$  (band I, 554 nm,  $\epsilon$  97.2; band II, 387 nm,  $\epsilon$  85.0) and  $\text{trans}(\text{O}_5\text{O}_6)\text{-}[\text{Co}(1,3\text{-pddadp})]^-$  (band I, 564 nm,  $\epsilon$  112.0; band II, 399 nm,  $\epsilon$  94.0) are similar to the spectrum<sup>2</sup> of  $[\text{Co}(1,3\text{-pdta})]^-$ . The absence of apparent splitting permits these complexes to be treated as pseudooctahedral with spin-allowed transitions to  $^1\text{T}_{1g}$  and  $^1\text{T}_{2g}$  states.

The absorption spectrum of the second isomer [ $\text{trans}(\text{O}_6)$ ] of  $[\text{Co}(1,3\text{-pddadp})]^-$  differs from those of the other complexes in two respects: the higher energy band (388 nm,  $\epsilon$  67.0) is more intense than the lower energy band, and the lower energy band (543 nm,  $\epsilon$  55.0) shows a pronounced shoulder on the lower energy side ( $\sim 612$  nm,  $\epsilon \sim 23$ ). This splitting of the  $\text{T}_{1g}(\text{O}_h)$  band indicates that the tetragonal field is enhanced, relative to the fields in the other complexes reported here. With the strain of the G rings relieved by the three-carbon diamine backbone, the in-plane field of 2 N and 2 O (of glycinate rings) is considerably stronger than the axial field of two propionate oxygens.

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**Supplementary Material Available:** A table of analytical data (1 page). Ordering information is given on any current masthead page.

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Institute of Chemistry  
Faculty of Science  
Svetozar Marković University  
Kragujevac 34000, Yugoslavia

Dušan J. Radanović  
Srećko R. Trifunović

Department of Chemistry  
University of Pittsburgh  
Pittsburgh, Pennsylvania 15260

Chris Maricondi  
Bodie E. Douglas\*