Reactions of dithizone with transition metal complexes of acetylacetone and oxine

A A M Aly* & A H Osman

Chemistry Department, Faculty of Science, Assiut University, Assiut, Egypt

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Synthesis of mixed acetylacetonato-dithizonato complexes of VO²⁺, Cr³⁺, Fe³⁺ and Co³⁺ as well as dithizonato-oxinate complexes of Co²⁺ and Ni²⁺ is described. On the basis of electronic spectral data, the mixed acetyl-acetonato complexes are assigned octahedral and the mixed oxinate complexes tetrahedral geometry. Photolysis of the complexes in chloroform solution is also investigated. Photooxidation through a reactive excited state of the charge transfer to solvent (CTTS) type is suggested. Thermal behaviour of the complexes has been also discussed.

Although dithizone has wide applications as an analytical reagent in the photometric analysis of metals, and it forms binary complexes with many metals¹,², reports are scarce on its mixed ligand complexes³. Further, among mixed ligand complexes of acetylacetone and of oxine, complexes with sulphur donors are scarce⁴⁻⁸. We report here the preparation and characterisation of mixed ligand transition metal complexes containing dithizone and acetylacetonate/oxinate as co-ligands.

Experimental

All the chemicals used were of analytical reagent grade. Dithizone (E. Merck) was used without further purification. The acetyl-acetonato and oxinate metal complexes, i.e., VO(acac)₂, Cr(acac)₃, Fe(acac)₃, Co(acac)₃, Co(ox)₂ and Ni(ox)₂ were prepared following recommended methods⁹,¹⁰.

(Acetylacetonato)(dithizonato)oxovanadium(IV)

and bis(acetylacetonato)(dithizonato)chromium(III)/iron(III)/Co(III)

A chloroform solution (10 ml) of dithizone (2.0 mmol) was added dropwise with continuous stirring to a chloroform solution (15 ml) of the metal acetylacetone (2.0 mmol). After stirring overnight, the solution was evaporated to about one-third the original volume, followed by the addition of petroleum ether. The precipitated complex was filtered, washed with a little chloroform and dried over P₄O₁₀.

The instruments used in the present work were: Perkin-Elmer 599 B recording spectrophotometer for IR spectra (KBr), Shimadzu UV-200 S spectrophotometer for UV spectra, Rayonet photochemical chamber reactor Modell RPR-100 for irradiation, and a thermobalance consisting of an electric furnace and a sample holder.

Results and discussion

The complexes were soluble in most of the organic solvents. Analytical data of the complexes are recorded in Table 1.

Table 1—Analytical data and colours of the complexes

<table>
<thead>
<tr>
<th>Complex (colour)</th>
<th>Found (Calc.)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C%  H%  N%</td>
</tr>
<tr>
<td>[VO(acac)(HDz)] (Brick red)</td>
<td>51.10 4.50 13.40</td>
</tr>
<tr>
<td>(Black) (51.31) (4.30) (13.29)</td>
<td></td>
</tr>
<tr>
<td>[Cr(acac)₂(HDz)] (Black)</td>
<td>54.55 4.82 11.12</td>
</tr>
<tr>
<td>(54.64) (4.98) (11.08)</td>
<td></td>
</tr>
<tr>
<td>[Cr(acac)(HDz)₁ (Brown)</td>
<td>56.33 4.45 16.81</td>
</tr>
<tr>
<td>(56.26) (4.41) (16.93)</td>
<td></td>
</tr>
<tr>
<td>[Fe(acac)₃(HDz)] (Brown)</td>
<td>54.02 4.81 11.20</td>
</tr>
<tr>
<td>(54.23) (4.94) (10.99)</td>
<td></td>
</tr>
<tr>
<td>[Co(acac)₂(HDz)] (Brown)</td>
<td>55.79 4.21 16.77</td>
</tr>
<tr>
<td>(55.94) (4.39) (16.83)</td>
<td></td>
</tr>
<tr>
<td>[Co(acac)(HDz)₁ (Dark violet)</td>
<td>53.88 4.99 10.90</td>
</tr>
<tr>
<td>(53.90) (4.91) (10.93)</td>
<td></td>
</tr>
<tr>
<td>[Co(acac)(HDz)₂ (Black)</td>
<td>55.55 4.25 16.86</td>
</tr>
<tr>
<td>(55.68) (4.37) (16.75)</td>
<td></td>
</tr>
<tr>
<td>[Co(ox)(HDz)] (Dark violet)</td>
<td>57.77 3.91 15.33</td>
</tr>
<tr>
<td>(57.64) (3.73) (15.27)</td>
<td></td>
</tr>
<tr>
<td>[Ni(ox)(HDz)] (Black)</td>
<td>57.51 3.82 15.31</td>
</tr>
<tr>
<td>(57.67) (3.73) (15.28)</td>
<td></td>
</tr>
</tbody>
</table>
The IR spectra of the complexes exhibit the characteristic bands of the ligands involved in the mixed ligand complexes. For the acetylacetonato-dithizonato mixed ligand complexes, it is inferred from the IR spectra that the bidentate coordination of acetylacetone is not altered upon further reaction with dithizonate since characteristic bands for νC=O and νC≡C appear at 1575-1590 and 2325-2335 cm⁻¹, and no band for free carbonyl is observed above 1600 cm⁻¹ (ref. 11).

In the spectrum of VO(acac)(HDz), νV=O is observed at 1015 cm⁻¹ indicating that the five coordinate geometry around V(IV) is retained as in the parent VO(acac)₂.¹²

The two complexes of oxine, viz., Co(ox)(HDz) and Ni(ox)(HDz) display νC=N and νC≡O at 1540 and 1120 cm⁻¹, respectively.

Chelation of the dithizonate moiety is evidenced by the appearance of νNH at 3220-3300 cm⁻¹ and νC=S at 840-850 cm⁻¹, typical of dithizonate coordination through S and N.¹³ A band located at 1320-1350 cm⁻¹ is attributed to νN=C of N-Ph bond.

The electronic spectra (chloroform solutions) of all the present complexes display an intense absorption band due to dithizonate moiety in the region 18000-19000 cm⁻¹ (refs 2, 3a). In the spectrum of VO(acac)(HDz) a band occurring at 20833 cm⁻¹ may be attributed to the dithizonate part. No d-d bands could be observed for this complex. The two bands appearing at 23255 and 37735 cm⁻¹ are probably due to CT and intraligand (acetylacetone) transitions, respectively.

The Cr(acac)₃(HDz) and Cr(acac)(HDz)₂ complexes show a band at ~16000 cm⁻¹ (A₂g → Tₐg). The transition A₂g → Tₐg occurs at 21739 cm⁻¹ for Cr(acac)₃(HDz), and at 23255 cm⁻¹ for Cr(acac)(HDz)₂. These two transitions are compatible with the expected pseudo-octahedral geometry around Cr(III). A band located at 37037 and 38461 cm⁻¹ for Cr(acac)₃(HDz) and Cr(acac)(HDz)₂, respectively, seems to correlate with a π-π* transition of acac⁻. The Cr(acac)₃(HDz) complex exhibits, in addition, a CT band at 30303 cm⁻¹, usually found in acetylacetone complexes.¹⁴

The two iron(III) complexes, Fe(acac)₃(HDz) and Fe(acac)(HDz)₂, display a broad structured dithizonate band at ~19000 cm⁻¹, which obscures the d-d bands. In addition, the two iron complexes show a band of high intensity at 37735-38461 cm⁻¹ (π-π* on acac⁻).¹⁴

The spectra of the Co(III) complexes show the transition A₁g → T₂g, typical of octahedral Co(III) complexes. It appears at 22222 and 23809 cm⁻¹ for Co(acac)₃(HDz) and Co(acac)(HDz)₂, respectively.

The two complexes show bands of medium intensity in the regions 32258-33333 cm⁻¹ and 38461-38666 cm⁻¹, which are presumably due to intraligand transition of acac⁻ and HDz⁻, respectively.

For the Co(ox)(HDz) complex, the dithizonate band at 18687 cm⁻¹ obscures the d-d bands of Co(II). The two bands at 23255 and 38461 cm⁻¹ are assigned to CT and intraligand transitions, respectively.

The band at 14925 cm⁻¹ in the Ni(ox)(HDz) complex is ascribed to the transition 3T₁(F)→3T₁(P)(ν₁) which is indicative of a tetrahedral coordination around Ni(II). The two bands at 29411 and 35713 cm⁻¹ are correlated with CT and intraligand transitions.

### Photochemistry

The spectral changes associated with photolysis of the complexes in chloroform solution at 300 nm show that the most prominent features in the absorption spectra decrease in intensity. By analogy with other photooxidations in halocarbon solvents, where solvent molecules act as electron acceptors, it is presumed that the complex becomes cationic; and chloride, abstracted from the solvent, acts as the counter anion. Such cations formed in the primary step by charge transfer to solvent (CTTS) are unstable and undergo further decomposition.¹⁶,¹⁸ Vogler et al.¹⁹ assumed a similar mechanism for the photooxidation of 1,2-dithiolen complexes of Ni(II), Pd(II) and Pt(II) in chloroform.

Irradiation of chloroform solutions of the present complexes at 365 nm gives rise to similar results, but the rate of conversion is low in comparison to that for irradiation at 300 nm. This behaviour seems to be characteristic of the reactivity of CTTS excited states.

### Thermal analysis

TGA analyses (heating rate 7°C/min) of the following complexes were carried out in the temperature range 100-400°C: VO(acac)(HDz), Cr(acac)₃(HDz), Fe(acac)₃(HDz), Co(acac)₃(HDz), and Co(ox)(HDz). The thermograms consisted of three decomposition steps. For the complexes VO(acac)(HDz), and Co(ox)(HDz) it was difficult to correlate the individual steps with decomposition products of reasonable constitution. However, the first mass losses of the complexes Cr(acac)₃(HDz) (190°C), Fe(acac)₃(HDz) (140°C) and Co(acac)₃(HDz) (170°C) were found to be commensurate with the elimination of one acetylacetone molecule and an azo group (N₂) (from the dithizonate moiety).

It is suggested that the mechanism of decomposi-
tion involves the initial loss of a proton from dithizonate to one of the two acetylacetones, which leaves as a neutral acetylacetone molecule; the primary dithizonate is thus transformed into a secondary dithizonate. Assuming elimination of the azo group, a 4-coordinate complex can be visualised at this stage.

References