Any oxygen liberated in the solution will combine rapidly with chromium(II) to give the dimeric species. It should be noted, however, that the observed dimer may well come about as the result of a competing "two-electron" oxidation to chromium(IV) and its subsequent reaction with chromium(II).

Correspondence

Evidence for Unidentate Acetylacetonate Ligand in $Na_2Pt(acac)_2Cl_2 \cdot 5H_2O$

Sir:

The crystal structure of $KPt(acac)_2Cl$[1] shows the coordination sphere around platinum to consist of the chloride ion, a bidentate acetylacetonate ion, and a unidentate acetylacetonate ion bonded through the γ-carbon. This unusual structure has prompted us to report our results on a similar compound,[2] $Na_2Pt(acac)_2Cl_2 \cdot 5H_2O$.

Our original interest was in finding a six-coordinate platinum(II) complex. Such compounds are rare,[3] but would be of interest thermodynamically and spectrochemically. The stoichiometry of this salt suggests that it could contain such an ion, since the acetylacetonate ion generally serves as a bidentate ligand. However, on the bases of spectral and chemical evidence, we believe that this compound contains two unidentate acetylacetonate ligands in both solid and aqueous phases.

The infrared spectra of transition metal acetylacetonates exhibit one, two, or three bands in the region between 1520 and 1600 cm.$^{-1}$ which are associated with the C=O (ν_1) and C=C (ν_2) stretching vibrations. In addition a band at about 780 cm.$^{-1}$ (ν_3) is presumably associated with the C–H out-of-plane bending vibration.[4-6] Pertinent frequencies of several of these acetylacetonates are compared with those of $KPt(acac)_2Cl$ and $Na_2Pt(acac)_2Cl_2 \cdot 5H_2O$ (Table I).

Table I

Frequencies in Wave Numbers, Cm.$^{-1}$

Compound	ν_1	ν_2	ν_3
$Al(acac)_3$	1600	1535	774
$Cu(acac)_2$	1580	1530	780
$Pt(acac)_2$	1565	1535	777
$KPt(acac)_2Cl$	1695 1653	Not reported	Not reported
$Na_2Pt(acac)_2Cl_2 \cdot 5H_2O$	1660 1640	1550 1540	

Since ν_1 for $Na_2Pt(acac)_2Cl_2 \cdot 5H_2O$ occurs at higher energy than those of the symmetrically coordinated ions, especially $Pt(acac)_2$, we conclude that the bonding is significantly different. We note that, while the split components of ν_1 are of somewhat lower energy than those of $KPt(acac)_2Cl$, it is still in the correct region for a carbonyl group in conjugation with a C=C linkage.[7] Significantly, there is no evidence of a band in the region of 780 cm.$^{-1}$, although $Pt(acac)_2$ shows a sharp and intense band in this region.

Further evidence for unidentate acetylacetonate ion is provided by the positive reaction of this compound with 2,4-dinitrophenylhydrazine, hydroxylamine, and $NaHSO_3$, reagents which are specific for a free carbonyl group. The analytical results for the dinitrophenylhydrazine derivatives show conclusively that *two* carbonyl groups are available for reaction. *Anal.* Calcd. for $Na_2[PtCl_2C_{22}H_{22}O_{10}N_8]$: C, 30.3; H, 2.53; Cl, 8.17; N, 12.9; Pt, 22.4. Found: C, 30.8; H, 2.62; Cl, 8.20; N, 13.1; Pt, 22.0. Similar reactions with $Al(acac)_3$ were attempted in alcohol–water mixtures with negative results.

Our results do not exclude an axially elongated octahedron possessing two thermodynamically and kinetically weak Pt–O bonds. Such a structure might account for the spectral and chemical evidence, but steric requirements of the acetylacetonate ion seem to preclude this possibility. Our results do not enable us to distinguish unequivocally between two γ-carbon-bonded acetylacetonate ligands, or two oxygen-bonded acetylacetonate ligands, or a combination of both. It is interesting to note that the reaction of phenylhydrazine with free acetylacetone produces N-phenylpyrazine. This fact alone, however, does not allow us to reach a firm conclusion with the present knowledge of template reactions.

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