Contact Ion Pairs in Solution and Infrared Evidence for the Structure of the Decacarbonyldichromium Dianion $[Cr_2(CO)_{10}]^{2-}$

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THE preparation of $[M_2(CO)_{10}]^{2-}$ anions (M = Cr, Mo, or W) which are said to be different from the anions of the same formula prepared earlier by Behrens[1] has been reported recently by Hayter.[2] The anions prepared by Behrens were reported to have the D_{4d} structure† on the basis of i.r. spectra near 5μ.[3] Because the spectra of the anions prepared by Hayter are more complex and include strong bands in the 1725—1825 cm.$^{-1}$ region, they are believed to have a structure of lower symmetry with bridging CO groups.[2,4]

We have examined the $5\ \mu$ i.r. spectra of $[Cr_2(CO)_{10}]^{2-}$ (Figure) prepared by both methods and find that they are identical. Thus, structural isomers do not appear to exist for this anion,‡ and presumably not for the Mo and W anions. We have also examined the i.r. and Raman spectra of the Cr anion in several solvents from 33 to 4000 cm.$^{-1}$. The bands (DMSO) at 1912s, 1883vs, and 1786s are assigned, respectively, to the B_2 equatorial, the E_1 equatorial, and the B_2 axial C–O stretching modes of the anion with D_{4d} symmetry. The Raman lines of this solution in this region are: 2008m, 1879vs, and 1809s cm.$^{-1}$; and these are assigned to the A_1 equatorial, E_2 equatorial, and A_1 axial C–O stretching modes, respectively. In addition, all of the spectral results at lower frequency for this anion in DMSO

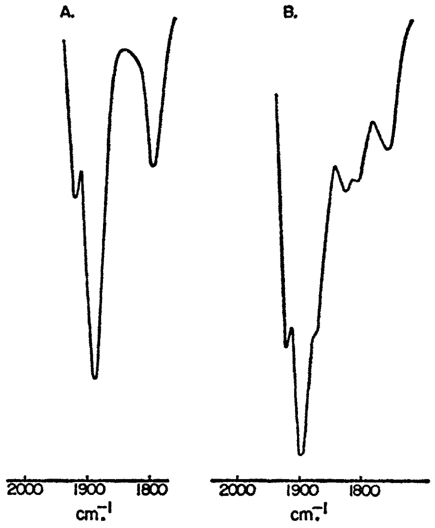

FIGURE. *The infrared spectrum of* $Na_2Cr_2(CO)_{10}$ *in the* $5{\cdot}3\mu$ *region*: [A, Dimethyl sulphoxide (DMSO), B, Tetrahydrofuran (THF)].

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† Metal–metal bond, no bridging CO groups, staggered equatorial CO groups.

‡ W. Beck (personal communication), has reported that Behrens and Linder have a new method of preparing these ions and that their 5μ i.r. spectra are now the same as those reported in this communication.

are also consistent with the D_{4d} structure and do not require the presence of bridging CO groups.

While the spectrum of $Na_2Cr_2(CO)_{10}$ in THF (Figure B) is more complex than that in DMSO, these results do not require the presence of a $[Cr_2(CO)_{10}]^{2-}$ anion with a geometric structure much different from the D_{4d} model. This spectrum is predominantly what one expects for an anion environment in which one *axial* CO is contact-ion paired with a Na^+ and the other CO groups have solvent molecules as nearest neighbours. We assume that solvent molecules as nearest neighbours do not significantly disturb the symmetry of a vibrating group, while an alkali metal ion among the nearest neighbours imposes sufficient additional (different) terms to the electrostatic and force fields to modify their effective symmetry.[5] These results are also consistent with the presence of smaller amounts of other solution environments for the essentially D_{4d} ion.

Ion pairing will occur when salts are dissolved in solvents of moderate-to-low dielectric constant. Alkali metal salts of metal carbonylate ions form contact ion pairs in THF (and other ethers) when the formal charge on the metal carbonyl group of one metal atom is unity or greater, and not when it is one-half or less. However, alkali metal salts of anions carrying unit charge do not form contact ion pairs in DMF, DMSO, and similar solvents. Ion pairing must be allowed for in interpreting the spectra of salts in solution.

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[4] U. Anders and W. Graham, *J. Amer. Chem. Soc.*, 1967, **89**, 539; J. Ruff, *Inorg. Chem.*, 1967, **11**, 2080.
[5] This assumption is supported by the results of a separate study of the vibration and ion pairing of a number of salts in a variety of solvents in progress in this laboratory: W. F. Edgell, R. Wright, and J. Lyford, jun., *J. Amer. Chem. Soc.*, to be published.