

has much less of a tendency to interact with either the metal or the thiocyanate ion.

In addition to the foregoing, an unexpected dividend was realized in practice in that the range of observed ISR values was expanded considerably, relative to that obtained with salicylic acid as the internal standard (see Table I). This tends to minimize the importance of errors in measurement, insofar as bonding mode assignments are concerned.

The data in Tables I and II clearly demonstrate, with one significant exception, the efficacy of using 1,4-dicyanobenzene as an internal standard for thiocyanate bonding mode determinations, irrespective of the calculational technique employed. The inflated ISR values exhibited by  $[\text{Pd}(\text{Me}_2\text{en})(\text{SCN})_2]$ , using both standards, are undoubtedly due to slightly nondegenerate, but unresolvable, in-phase and out-of-phase  $\nu_{\text{CN}}$  stretching bands which artificially enhance the half-bandwidth. The complex has unequivocally been shown to contain S-bound thiocyanates by  $^{14}\text{N}$  NQR measurements.<sup>6</sup> This illustrates the major weakness of the ISR technique, i.e., the problems encountered in dealing with overlapping, poorly resolved  $\nu_{\text{CN}}$  bands. Although the ISR values to be compared should be determined by the same calculational technique, it is true, nonetheless, that, with the exception noted, M-SCN complexes generally exhibit ISR values <10, using 1,4-dicyanobenzene as the internal standard, while those of M-NCS complexes generally exceed 20. These values roughly reflect the salicylic acid ISR range limits multiplied by the ISR of salicylic acid itself (relative to 1,4-dicyanobenzene).

For optimization of the precision and accuracy of the measurements, the standard and complex  $\nu_{\text{CN}}$  peak should cover as much as possible of the 80-20% transmittance range but should not exceed these limits. The cut-and-weigh method encounters more problems in dealing with samples containing small amounts of isomeric impurities, since they enhance absorption in the wings of the main peak and are thereby included in determining the weight of the peak. Unless these isomeric impurities affect  $\Delta\nu_{1/2}$  and/or are a large percentage of the sample by weight, the calculation method (eq 1) is largely unaffected, since the peak is assumed to be Lorentzian in shape. The extra significant figure shown for the Nujol mull ISR values (Table I) simply reflects the larger sample size used in their preparation. The Nujol method is advantageous in that it avoids the possibility of pressure-<sup>2</sup> or KBr-induced<sup>12</sup> linkage isomerization.

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**Registry No.** 1,4-Dicyanobenzene, 623-26-7.

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### Gas Chromatographic Separation of Facial and Meridional Tris(1,1,1-trifluoro-2,4-pentanedionato)molybdenum(III)

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Among the known oxidation states of molybdenum, the paucity of chemical information related to Mo(III) is remarkable, especially when contrasted with the rich chemistry of Cr(III). We have identified fewer than 30 isolated and

thoroughly characterized complexes of molybdenum(III).<sup>1-19</sup> Most of these are monomeric six-coordinate high-spin ( $\mu(\text{eff}) = 3.84$ ) species readily described within the confines of crystal field theory. It has commonly been assumed that ligand substitution reactions of molybdenum(III) are slow, by analogy with the known chemistry of chromium(III), and under the assumption that Basolo and Pearson's argument relating crystal field splitting to the activation energy of dissociative processes may be applied to the  $4d^3$  electronic configuration as readily as it has been applied to the  $3d^3$  system. Indeed, Wentworth<sup>20</sup> dismissed the biological role of Mo(III) largely

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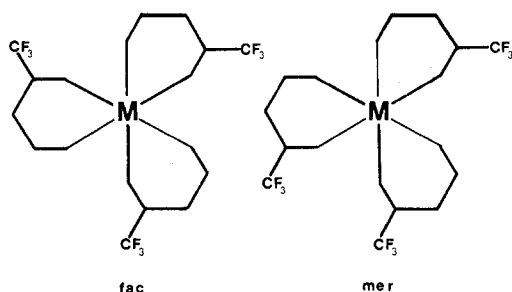


Figure 1.

on the basis of its presumed substitution inertness. Yet we have found only two experimentally determined ligand substitution rates for molybdenum(III). We report further evidence for the substitution inertness of Mo(III) in terms of the facile gas phase separation of the *fac* and *mer* isomers of tris(1,1,1-trifluoro-2,4-pentanedionato)molybdenum(III) ( $\text{Mo}(\text{tfa})_3$ ).

Uncharged metal complexes of 1,1,1-trifluoro-2,4-pentanedione are rather volatile and can be analyzed by gas chromatography.<sup>21</sup> This method has been used to separate and quantify mixtures of metal ions. An example is the trace analysis of rhodium through formation and gas chromatography of  $\text{Rh}(\text{tfa})_3$ .<sup>22</sup>

Complexes such as  $\text{Cr}(\text{tfa})_3$  exist in facial and meridional forms (Figure 1). These geometrical isomers differ in polarity and have occasionally been separated by gas chromatography. Sievers<sup>23</sup> separated the isomers of  $\text{Cr}(\text{tfa})_3$  on a column of 5% silicon grease at 115 °C. Kutal and Sievers<sup>24</sup> expanded this work to measure the rate of isomer conversion in the gas phase.

Gas chromatography provides an especially convenient method for separating geometrical isomers of an air-sensitive complex such as  $\text{Mo}(\text{tfa})_3$ .

Though easily prepared from readily available starting materials, molybdenum(III) complexes with  $\beta$ -ketoenolate ligands are extremely air sensitive; tris(2,4-pentanedionato)molybdenum(III), when dry, will spontaneously burst into flame upon exposure to atmospheric oxygen. Under controlled conditions, oxidation proceeds to nonvolatile products of the type  $(\text{Mo}(\text{L})_2\text{O})_2\text{O}$  (where L is a  $\beta$ -ketoenolate ligand). Within our procedures, unavoidable contact with air produced some of these oxidation products which are readily separated from the tris( $\beta$ -ketoenolate) molybdenum(III) complexes by gas chromatography and readily distinguished from the tris complexes by means of the electronic spectra.

A freshly prepared sample of tris(1,1,1-trifluoro-2,4-pentanedionato)molybdenum(III) ( $\text{Mo}(\text{tfa})_3$ ) was dissolved in deaerated benzene and chromatographed on a 6-ft 2% SE-30 on Chromasorb G column at 158 °C. Two symmetrical peaks, well separated from the benzene peak, were observed with retention times of 5 and 10 min, at a carrier gas flow rate of 20 mL/min. The use of a thermal conductivity detector allowed the collection of the observed fractions. The complexes condensed into glass tubes attached to the end of the column and were transferred to a glovebag under nitrogen, and the tubes were washed out with deaerated benzene. The electronic spectra of these solutions are identical with the spectrum of  $\text{Mo}(\text{tfa})_3$ .

The *fac* isomers of  $\text{Cr}(\text{tfa})_3$  and  $\text{Co}(\text{tfa})_3$  are much more soluble in ethanol than are the *mer* isomers.<sup>25</sup> Accordingly,

a sample of  $\text{Mo}(\text{tfa})_3$  was suspended in deaerated ethanol for several days. The residue from filtration was dissolved in benzene and chromatographed as before. A single peak at 10-min retention time was observed, suggesting that, in the original chromatogram, *fac*- $\text{Mo}(\text{tfa})_3$  was eluted with a retention time of 5 min, and *mer*- $\text{Mo}(\text{tfa})_3$  was eluted at 10 min.

An X-ray powder pattern was taken of the proposed *mer*- $\text{Mo}(\text{tfa})_3$  to confirm its identity. Samples were finely ground under nitrogen in a glovebag and packed in a capillary which was sealed with wax. The powder diffraction pattern of the proposed *mer*- $\text{Mo}(\text{tfa})_3$  can be compared with the reported patterns for *fac*- and *mer*- $\text{M}(\text{tfa})_3$ ,<sup>25</sup> where M = Cr, Co, or Rh. The *mer* complexes have three major lines at  $d = 9.95$ – $10.15$ ,  $6.48$ – $6.51$ , and  $3.87$ – $4.03$  Å. The *fac* complexes do not display all three of these major lines, and none has a  $d$  greater than 9.13 Å. The  $\text{Mo}(\text{tfa})_3$  diffraction pattern contains major lines at 10.04, 6.65, 5.56, and 4.01 Å, which correspond rather closely to the patterns for other *mer* complexes. Since the *fac* complexes have their most intense line at  $d = 7.13$ – $7.43$  Å and there is no corresponding line for the  $\text{Mo}(\text{tfa})_3$  complex, the  $\text{Mo}(\text{tfa})_3$  sample, thus, is the *mer* isomer. Moreover, the melting point of the complex, which elutes at 10 min, lies in the range 153–156 °C, and that of the isomer, which elutes at 5 min, lies in the range 122–128 °C.<sup>26</sup> These observations are also consistent with the reported melting points of other  $\text{M}(\text{tfa})_3$  complexes, in which the melting point of the *fac* isomer is uniformly lower than that of the *mer* isomer.<sup>25</sup>

These data suggest that the more polar *fac* isomer is eluted before the *mer* isomer, in contrast with previous experience.<sup>24</sup> The conditions employed in our separation are expected to depend more strongly on differences in volatility between the separated species<sup>26</sup> than on the interaction of either isomer with the chromatographic medium. We suggest, however, that the separation may also depend on the greater solubility of the less polar *mer* isomer in the stationary phase (silicone grease).

Assuming that the detector response to *fac*- and *mer*- $\text{Mo}(\text{tfa})_3$  is the same, we can calculate the distribution of isomers from the peak areas in the chromatogram. At room temperature, therefore,  $\text{Mo}(\text{tfa})_3$  is 11.5% *fac* isomer. This is considerably lower than the 25% predicted on a statistical basis. On the other hand,  $\text{Cr}(\text{tfa})_3$  and  $\text{Co}(\text{tfa})_3$  are only about 17–20% *fac* isomer at room temperature.<sup>24</sup>

## Experimental Section

Tris(1,1,1-trifluoro-2,4-pentanedionato)molybdenum(III) was prepared by the method of Dunne and Cotton.<sup>27</sup>

Gas chromatography was performed on a Varian-Aerograph A90-P3 chromatograph equipped with thermal conductivity detectors. Carrier gas (He) flowed through the 6-ft stainless-steel column packed with 2% SE-30 on Chromasorb G (100–120 mesh) at a rate of 20 mL/min. The injector temperature was 180 °C; that of the column was 158 °C, and that of the detector was 199 °C.

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**Registry No.** *fac*- $\text{Mo}(\text{tfa})_3$ , 72746-46-4; *mer*- $\text{Mo}(\text{tfa})_3$ , 72746-47-5.

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