and Hickford,[13] might also contain rhenium chloride species in oxidation states of less than 3+. Accordingly we prepared these derivatives according to the method of Fergusson and Hickford[13] and recorded their electronic and/or vibrational spectra. For all three products their infrared spectra (4000–400 cm^{-1}), recorded as Nujol mulls, revealed bands characteristic of the 2,2',2''-terpyridinium cation[14] and 2,2',2''-terpyridyl.

The mull electronic specta of the solids prepared by the method which were described as affording Re$_3$Cl$_9$-(terpy)$_{1.33}$ and Re$_3$Cl$_9$(terpy)$_2$[13] did not show a low-energy absorption band near 8000 cm^{-1} and resembled closely the spectra of the reduced species isolated from the rhenium(III) chloride–2,2'-bipyridyl systems.

(13) J. E. Fergusson and J. H. Hickford, *Inorg. Chim. Acta*, **2**, 475 (1968).
(14) In particular, a fairly intense band at 1540–1535 cm^{-1} is characteristic of the cation and is not shown in the spectra of complexes of 2,2',2''-terpyridyl.

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Spin-Forbidden Transitions in Chromium–Sulfur Chelates

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For the d^3 chromium system, crystal field theory predicts in O_h symmetry three low-energy spin-forbidden transitions, $^2E \leftarrow {}^4A_2$, $^2T_1 \leftarrow {}^4A_2$, and the $^2T_2 \leftarrow {}^4A_2$, all described in orbital notation as $t_2^3 \rightarrow t_2^3$ transitions. However, the small radiative probability of these transitions frequently precludes observing them in solution absorption spectra. Use of dilute single-crystal samples to obtain better resolution and increased absorbance is limited by the availability of transparent isomorphous host lattice materials. Polymer solvent media may provide a suitable compromise between liquid solution and solid solution determination of spin-forbidden transitions.

Reported below are the energies of these transitions in five tris chromium(III) complexes: diethyldithiophosphate, dtp; dimethyldithiocarbamate, dmtc; diethyl dithiocarbamate, detc; methyl xanthate, mxan; and ethyl xanthate, exan. The $^2T_2 \leftarrow {}^4A_2$ transition has not been previously located for these complexes. An explanation of the extra band in the region of the $^4T_1$ band for Cr(dtp)$_3$ is given. The emission spectra for the complexes are also reported, clarifying some earlier results.

Experimental Section

Synthesis.—The sulfur chelates were synthesized by literature methods.[1-3] Purity was determined by melting point, thin layer chromatography, and C–H analysis. Compounds were stored at 0° after purification and repurified just before use.

Glassy solvents used were EPA [ether–isopentane–ethanol (5:5:2)] and EPA–CHCl$_3$ (2:1). Polymer samples were made by dissolving the complexes in partially polmerized methyl methacrylate syrup. Further polymerization was done thermally (75° until firm and then 100° for 2 days). The samples were stored under vacuum until use.

The Cr(dmtc)$_3$ and Cr(exan)$_3$ crystals diluted into the corresponding indium host chelate were grown from reagent grade acetone. The Cr(dtp)$_3$–In(dtp)$_3$ crystals were obtained as flakes from 95% ethanol.

Results and Discussion

The absorption spectra of Cr(mxan)$_3$ and Cr(exan)$_3$ in polymer and crystalline hosts contain resolved weak bands at 18.1 and 18.4 kK and shoulders at 13.0 and 13.9 kK superimposed upon the $^4T_2 \leftarrow {}^4A_2$ transition. The lowest energy transition is assigned as the $^2E \leftarrow {}^4A_2$ transition consistent with the emission spectrum. The shoulder at 13.9 kK is tentatively assigned as the $^2T_1 \leftarrow {}^4A_2$ transition. On the basis of their sharpness, intensity, and the Sugano–Tanabe diagram, the two narrow resolved bands at 18.1 and 18.4 kK are assigned as the trigonally split components (^2E and $^2A_2$) of the $^2T_2$ state.

The emission from these complexes (Table I) is nar-

TABLE I
77°K EMISSION MAXIMA (KK) AND LIFETIMES (μSEC)

Compound	Crystal		Polymer^a	
	$\bar{\nu}$	τ	$\bar{\nu}$	τ
Cr(dmtc)$_3$	11.9	10^b	12.5	128
Cr(detc)$_3$	11.9	34^b	12.5	120
Cr(maxn)$_3$	12.5	50^c	12.7	360
Cr(exan)$_3$	12.8	46^c	12.7	350

^{a} Unchanged in glassy solution. ^{b} Independent of concentration to 0.1% Cr^{3+}–In(dmtc)$_3$. ^{c} Independent of concentration to 0.1% Cr^{3+}–In(exan)$_3$.

row ($\bar{\nu}_{1/2} = 0.410$ kK) and overlaps with the $^2E \leftarrow {}^4A_2$ absorption band and therefore is assigned as a $^2E \leftarrow {}^4A_2$ *phosphorescence*.[4] The emission decay curve is exponential and gives a lifetime (Table I) consistent with this assignment.

The 83°K absorption spectrum for the Cr(dmtc)$_3$ dilute crystal and polymer samples indicates weak spin-forbidden absorption bands at 12.7, 13.0, 14.0, 18.3, and 18.6 kK. In glassy solution the bands at 12.7, 13.0, and 14.0 were not observed. By analogy to the xanthates the bands at 12.7 and 14.0 kK are assigned as the $^2E \leftarrow {}^4A_2$ and $^2T_1 \leftarrow {}^4A_2$ transitions, respectively. In like manner the transitions observed at 18.3 and 18.6 kK are assigned as the trigonally split components of the $^2T_2 \leftarrow {}^4A_2$ transiton.

The emission maximum for Cr(dmtc)$_3$ and Cr(detc)$_3$ (Table I) shows a small Stokes shift, but the lifetime (Table I) is 10–15 times greater than usually observed for the Cr(III) fluorescence ($^4T_2 \rightarrow {}^4A_2$).[5] Further the emission half-width (0.80 kK) is much too narrow for

(1) C. K. Jørgensen, *J. Inorg. Nucl. Chem.*, **24**, 1571 (1962).
(2) F. Galsbol and C. E. Schaffer, *Inorg. Syn.*, **10**, 42 (1968).
(3) D. E. Coldbery, W. C. Fernelius, and M. Shamma, *ibid.*, **6**, 142 (1960).
(4) P. Cancellieri, E. Cervone, C. Furlani, and G. Sartori, *Z. Phys. Chem.* (*Frankfurt am Main*), **62**, 35 (1968).
(5) G. B. Porter and S. Chen, *J. Amer. Chem. Soc.*, **92**, 2189 (1970).

the emission to be classified as a fluorescence.[6] On the basis of the half-width and lifetime, the emission is classified as a phosphorescence, $^2E \rightarrow {}^4A_2$. The Stokes shift is attributed to a significant perturbation of the ^2E state by the close-lying $^4T_2$ state. The observation of only one emission maximum for the dithiocarbamates contrasts the two maxima reported by Cancellieri and coworkers.[4] Measurements on $Cr(dmtc)_3$, described below, suggest that the 11.0-kK maximum ($\bar{\nu}_{1/2} = 2.0$ kK) observed by these workers is due to an impurity. An undiluted powder purified only by recrystallization gave a broad emission ($\bar{\nu}_{1/2} = 2.0$ kK) in the solid state centered at 10.5 kK but only the narrower emission ($\bar{\nu}_{1/2} = 0.80$ kK) in the EPA–CHCl$_3$ glass. After this powder was vacuum sublimed, only the narrower emission was obtained from the solid. A brown residue that was insoluble in organic and inorganic solvents remained in the apparatus. Infrared scans of this powder before and after sublimation were identical as were the melting points and thin layer plates (silica gel). The C, H, and N analyses did indicate that the presublimed powder was higher in per cent C and H but lower in per cent N than the theoretical values.

The 83°K absorption spectrum of $Cr(dtp)_3$ shows weak bands at 13.1, 13.7, and 17.4 kK in polymer and crystal. In addition two peaks are observed at 19.2 and 18.6 kK. Jørgensen[1] has assigned the 18.6-kK peak as a spin-forbidden transition, while others have suggested that both peaks are components of the $^4T_1$ state.[7] The bands at 13.1 and 13.7 kK are assigned as the $^2E \leftarrow {}^4A_2$ and $^2T_1 \leftarrow {}^4A_2$ transitions, respectively. Cancellieri[4] observed weak absorption bands for this complex in hydrocarbon solvents at 11.1 and 11.8 kK and assigned them to the $^2E \leftarrow {}^4A_2$ transition. We also observed these bands in hydrocarbon solvents but only when no solvent reference was used. These bands, which are not observed in CCl$_4$, can be assigned as fourth-order C–H stretch vibrations in the solvent. The weak band at 17.4 kK is, by analogy to the xanthate and dithiocarbamate complexes, one of the two transitions to the trigonally split $^2T_2$ state. The other component may be the band at 18.6 kK on the peak of the $^4T_1 \leftarrow {}^4A_2$ absorption band.

Emission at 83°K from $Cr(dtp)_3$ could not be detected using photomultiplier detection or photographic detection with a Spex 1800 spectrograph.

Glassy solution emission intensities observed for these chelates at 77°K are generally weak, suggesting very low quantum yields. No chemical evidence for any irreversible photolysis in glassy solution was detected under these excitation conditions, although some decomposition was observed for solid material allowed to stand for periods of weeks. Steady irradiation of the $Cr(exan)_3$ and $Cr(mxan)_3$ complexes in EPA and polymer glasses at any temperature greater than 77°K produced an exponential decrease in the emission intensity with time. After 6–8 min of irradiation an equilibrium intensity was reached. This decrease in intensity was independent of excitation wavelength from 250 to 620 nm. The initial intensity could be recovered by allowing the sample to remain in the dark. The decrease in intensity was not observed when the

sample was in direct contact with liquid nitrogen (77°K). Since the emission intensity and lifetime of these two complexes is temperature dependent,[8] experiments were performed to eliminate the possibility that excitation radiation warmed the sample. First, a copper–constantan thermocouple was placed directly into the irradiated portion of the sample. No temperature change was detected during irradiation. Finally, a sample of $Cr(aca)_3$ in EPA was irradiated under the same conditions and the emission monitored. The emission intensity of this complex is temperature dependent.[9] No decrease in intensity with exposure time was observed for $Cr(aca)_3$. The fact that the emission intensity decrease is observed in polymer as well as EPA eliminates a solvent–complex interaction. This phenomenon cannot be explained at present.

(6) G. B. Porter and H. L. Schlafer, *Z. Phys. Chem. (Frankfurt am Main)*, **37**, 109 (1963).

(7) J. R. Wasson, S. J. Wasson, G. M. Woltermann, *Inorg. Chem.*, **9**, 1576 (1970).

(8) K. DeArmond and W. Mitchell, unpublished results.

(9) W. Targos and L. S. Forster, *J. Chem. Phys.*, **44**, 4342 (1966).

Antimony-121 and Iron-57 Mössbauer Effect in Substituted Iron Pentacarbonyls

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Although the ^{57}Fe Mössbauer effect in $Fe(CO)_5$ and its derivatives has been the subject of many investigations over the past 8 years[1-7] and although the mono- and disubstituted $(C_6H_5)_3P$ compounds have been studied,[1-3] Mössbauer spectra of the analogous $(C_6H_5)_3$-As and $(C_6H_5)_3Sb$ derivatives have not been reported. As the Mössbauer effect can be observed with ^{121}Sb,[8,9] the latter compounds can be studied by a double Mössbauer experiment, a technique which has given interesting results for compounds containing Fe–Sn bonds.[10,11] We report here the ^{57}Fe Mössbauer spectra of the series $(C_6H_5)_3MFe(CO)_4$ and $((C_6H_5)_3M)_2Fe(CO)_3$, where M is P, As, or Sb, and the ^{121}Sb spectra of the two antimony derivatives.

(1) R. L. Collins and R. Pettit, *J. Chem. Phys.*, **39**, 3433 (1963).

(2) R. L. Collins and R. Pettit, *J. Amer. Chem. Soc.*, **85**, 2332 (1963).

(3) R. H. Herber, R. B. King, and G. K. Wertheim, *Inorg. Chem.*, **3**, 101 (1964).

(4) L. Korecz and K. Burger, *Acta Chim. (Budapest)*, **58**, 253 (1968).

(5) E. Fluck, in "Chemical Applications of Mössbauer Spectroscopy," V. I. Goldanskii and R. H. Herber, Ed., Academic Press, New York, N. Y., 1968.

(6) W. R. Cullen, D. A. Harbourne, B. V. Liengme, and J. R. Sams, *Inorg. Chem.*, **8**, 1464 (1969).

(7) R. E. Dessy, J. C. Charkoudian, T. P. Abeles, and A. L. Rheingold, *J. Amer. Chem. Soc.*, **92**, 3947 (1970).

(8) S. L. Ruby in "Mössbauer Effect Methodology," Vol. 3, I. J. Gruverman, Ed., Plenum Press, New York, N. Y., 1967.

(9) G. G. Long, J. G. Stevens, R. J. Tullbane, and L. H. Bowen, *J. Amer. Chem. Soc.*, **92**, 4230 (1970).

(10) D. E. Fenton and J. J. Zuckerman, *ibid.*, **90**, 6226 (1968).

(11) W. R. Cullen, J. R. Sams, and J. A. J. Thompson, *Inorg. Chem.*, **10**, 843 (1971).