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Resonance Raman Spectroscopy of Tetrahedral Cobalt(II) Thiourea and Mercaptide Complexes

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Raman spectra have been obtained for $Co(TU)_2X_2$ (TU = thiourea, X = Cl, Br, I), $Co(TU)_4^{2+}$, $Co(DETU)_2Cl_2$ (DETU = diethylthiourea), $Co(DESU)_2Cl_2$ (DESU = diethylselenourea), $Co(SPh)_4^{2-}$ (SPh = phenylmercaptide), and $Co(SC(CH_3)_2CH_2NH_2)_2$ using a variety of laser wavelengths, from the red to the near-UV region. Cobalt–ligand modes were assigned, and they were observed to be enhanced via the visible transitions. Enhancement factors for Co–S modes were comparable to those previously obtained for cobalt–imidazole modes and give promise for monitoring Co–S vibrations in cobalt(II)-substituted proteins with mercaptide ligands. The near-UV S → Co charge-transfer transition gives modest enhancements for Co–S modes and also enhances C–S modes, which are not resonant with the visible transitions. Excitation profiles for the symmetric cobalt–ligand modes of $Co(TU)_2Cl_2$ and $Co(TU)_2Br_2$ unexpectedly show peaks at ~520 nm, in a region of the spectrum devoid of absorption. An interference mechanism is proposed to account for these off-resonance peaks.

Introduction

As part of a program to evaluate the applicability of resonance Raman spectroscopy to cobalt(II)-substituted metalloproteins,[2] we have examined some complexes with cobalt(II)–sulfur bonds. Although the parity-forbidden "d–d" bands of transition-metal complexes are not ordinarily effective in providing resonance enhancement of Raman modes,[3] substantial enhancements have been observed[2,4,5] for cobalt(II)–ligand modes in resonance with the moderately intense visible bands of tetrahedral Co^{II} complexes. These same visible bands have served as spectroscopic handles for monitoring interactions at the metal-binding site of zinc proteins[6,7] and recently also of copper proteins[8] after substitution with Co^{II}.

Imidazole appears to be the most common ligand in metalloproteins, and useful enhancements of cobalt(II)–imidazole stretching modes are observed in complexes of roughly tetrahedral geometry.[2] Cysteine mercaptide coordination is established in liver alcohol dehydrogenase (LADH)[9] and inferred in metallothionen[10] and at the "type I" site of copper proteins.[8] Accordingly it is of interest to examine the characteristics of cobalt(II)–sulfur Raman modes.

Mercaptide complexes of Co^{II} are oxidatively and photolytically unstable and we have found it difficult to obtain acceptable Raman spectra, although preliminary data are reported herein for the bis((β-mercapto-β′,β″-dimethylethyl)amino)[11] and tetrakis(phenylmercapto)[12] complexes. Thiourea complexes are much more stable and we have been able to investigate them more thoroughly. While thiourea and mercaptide sulfur might be thought to be quite different chemically, they appear to have similar optical electronegativities; the electronic spectra of cobalt(II)–thiourea complexes[13] show d–d and charge-transfer bands that are close in energy to those found in mercaptide complexes.[11] Also the Co–S distances are similar for cobalt(II)–thiourea[14] and –mercaptide[11] bonds as are the Co–S stretching frequencies (vide infra).

Table I. Cobalt-Sulfur and Cobalt-Halide Stretching Frequencies (cm^{-1})[a]

	Co-S		Co-X	
	sym	asym	sym	asym
$Co(TU)_2Cl_2$	247 (252)[b]		294 (295)	315 (316)
$Co(TU)_2Br_2$	257 (251)	270 (276)	183 (190)	222 (235)
$Co(TU)_2I_2$	262 (250)	275 (268)	175 (184)	217 (204)
$Co(DETU)_2Cl_2$[c]	238		*d*	
$Co(DESU)_2Cl_2$[c]	165	190	*d*	
$Co(TU)_4(NO_3)_2$	230	257, 300 (261, 280, 297)		
$Co(SPh)_4(PPh_4)_2$	192	203, 215		
$Co(S\text{-}N)_2$[e]	245			

[a] All frequencies were measured in K_2SO_4 pellets or Nujol mulls. [b] Values in parentheses are infrared frequencies, from ref 19. [c] DETU = diethylthiourea, DESU = diethylselenourea. [d] Metal-halide stretches were obscured by ligand modes. [e] S-N = (β-mercapto-β′,β″-dimethylethyl)amine.

Experimental Section

Thiourea and hydrated $CoCl_2$, $CoBr_2$, and $Co(NO_3)_2$ were obtained from Fisher Scientific; CoI_2 was obtained from the Aldrich Chemical Co. These reagents were used as received. $Co(TU)_2X_2$ (X = Cl, Br, I; TU = thiourea) and $Co(TU)_4(NO_3)_2$ were prepared according to published procedures.[15] Dark blue crystals of $Co(DETU)_2Cl_2$ (DETU = diethylthiourea) formed when a warm solution of 1.32 g (0.01 mol) of DETU and 1.18 g (0.005 mol) of $CoCl_2·6H_2O$ in 40 mL of absolute ethanol was cooled to 5 °C.[13] The product was collected by filtration and dried in air. We did not ascertain whether the triclinic or monoclinic crystalline modification[16] of this complex was obtained. Diethylselenourea (DESU) was prepared by a published method.[17] After purification by recrystallizations from benzene–petroleum ether mixtures, the white product melted to a red liquid at 87–89 °C (lit. mp 88–90 °C). The addition of 0.73 g (0.004 mol) of $CoCl_2·6H_2O$ in 40 mL of 2-propanol resulted in an immediate change in color to green. After the green solution was filtered and maintained at 5 °C for 2 days, it deposited green crystals of $Cu(DESU)_2Cl_2$. The product was collected by filtration and dried in air. Anal. Calcd for $C_{10}H_{24}N_4Cl_2Se_2Co$: C, 24.61; H, 4.96; N, 11.48. Found: C, 25.03; H, 4.98; N, 11.68. A structural study of this complex is in progress. It crystallizes as rectangular prisms in the monoclinic space group $P2_1$ with a = 10.457 (3) Å, b = 15.164 (3) Å, c = 24.431 (8) Å, and β = 92.34 (3)°.[18] $Co(SC(CH_3)_2CH_2NH_2)_2$ was prepared as described previously.[11] $[Co(SPh)_4](PPh_4)_2$ (Ph = phenyl) was a generous gift of Professor Dimitri Coucouvanis.

Resonance Raman spectra were obtained mainly with solid samples, mixed with K_2SO_4 (50%), the sulfate serving as an internal standard. The mixtures were pressed into pellets and mounted on a spinning sample holder. The laser sources were a Spectra Physics 170 Ar^+ laser with UV optics, a Coherent Radiation 590 tunable dye laser, and a Coherent Radiation 52 Kr^+ laser. The spectra were obtained with Spex 1401 and Cary 82 spectrometers. Absorption spectra of evaporated films and acetone solutions were obtained with a Cary 118 spectrometer.

Results and Discussion

Cobalt–Sulfur Stretching Frequencies. Table I summarizes the cobalt(II)–ligand stretching frequencies observed in the low-frequency Raman spectra for the compounds included in this study. Assignment to metal–ligand modes was confirmed by the observation of resonance enhancement in the visible absorption bands.

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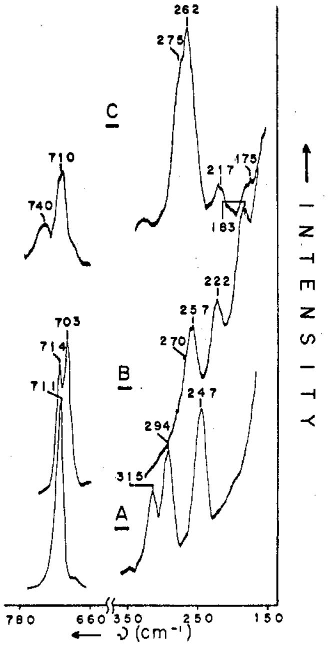

Figure 1. Raman spectra of $Co(TU)_2X_2$ in K_2SO_4 pellets: A, X = Cl, 568.2-nm excitation; B, X = Br, 568.2-nm excitation; C, X = I, 647.1-nm excitation. Conditions: spectral slit width 13 cm^{-1}, scan rate 0.2 cm^{-1}/s, time constant 10 s, sensitivity 2 × 10^3 Hz.

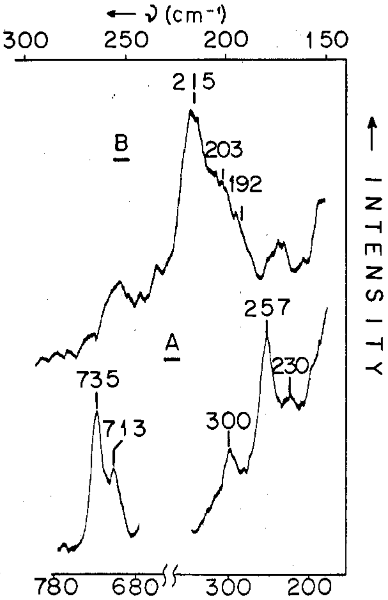

Figure 2. Raman spectra of (A) $Co(TU)_4(NO_3)_2$ and (B) $Co(SPh)_4(PPh_4)_2$, in K_2SO_4 pellets with 568.2-nm excitation. Conditions: spectral slit width 13 (A) and 1.5 (B) cm^{-1}; scan rate 0.2 (A) and 0.1 (B) cm^{-1}/s; time constant 10 (A) and 2 (B) s; sensitivity 10 (A) and 5 × 10^3 (B) Hz.

For the bis(thiourea)–dihalide complexes (whose Raman spectra are shown in Figure 1), the Raman frequencies agree reasonably well with the IR frequencies reported by Adams and Cornell.[19] (The discrepancies, of up to 13 cm^{-1}, might result from solid-state effects.) The cobalt(II)–halide frequencies decrease with increasing halide mass, as expected. For the bromide and iodide complexes, the two expected Co^{II}–S modes can be resolved, as shown in Figure 1, but in the chloride complex only one band is observed, presumably because the two modes are accidentally degenerate. (The two Co^{II}–X frequencies are also more closely spaced in the chloride than in the bromide or iodide complexes.)

The Co^{II}–S frequencies increase from chloride to bromide to iodide. For the chloride and bromide this increase can be explained in part by a crossing over of the cobalt(II)–halide modes, which push the Co^{II}–S frequencies down in the chloride but up in the bromide. The increase between bromide and iodide, however, implies a strengthening of the Co–S bonds. A concomitant strengthening of the cobalt–halide bonds is likewise indicated by the relatively high Co–I frequencies[20] only 5–8 cm^{-1} lower than the Co–Br frequencies. This may be an example of synergism between two "soft" bases, thiourea and iodide, bound to the same metal center.[21]

The diethylthiourea–dichloro complex also shows a single Co–S Raman band, at 238 cm^{-1}, shifted down by 9 cm^{-1} from that of $Co(TU)Cl_2$, consistent with a larger effective mass of the substituted thiourea ligand. The diethylselenothiourea complex shows two Co–Se bands, at 165 and 190 cm^{-1}. The tetrakis(thiourea) complex gives three Co–S bands, at 230, 257, and 300 cm^{-1}, as shown in Figure 2. The latter two are also seen in the infrared spectrum,[19] as is another band, at 280 cm^{-1}. The crystal structure of the complex shows substantial distortions from tetrahedral symmetry.[22] Adams and Cornell[19] assigned the three IR bands to the three components of the asymmetric stretching mode, split by symmetry lowering. The Raman band at 230 cm^{-1} is assignable as the breathing mode.

The amino–mercapto complex bis((β-mercapto-β′,β″-dimethylethyl)amino)cobaltate(II) gave poor-quality Raman spectra but did, however, show a definite resonance-enhanced broad band at 245 cm^{-1}, which we assign to the Co–S modes. The coincidence of this frequency with that of $Co(TU)_2Cl_2$ strengthens the impression that cobalt–mercaptide and cobalt–thiourea bonding are similar. The tetrakis(benzenethiolate) complex gave a somewhat better spectrum, with a broad band at ~200 cm^{-1}. At higher resolution this band showed at least three identifiable components, at 192, 203, and 213 cm^{-1}, as shown in Figure 2. These frequencies are substantially lower than those of $Co(TU)_4^{2+}$, reflecting both the greater effective mass of benzenethiolate and the longer Co–S distance found in $Co(SPh)_4^{2-}$ (2.346 Å[23] vs. 2.298 Å[22] in $Co(TU)_4^{2+}$).

Carbon–Sulfur Stretching Modes. In addition to the cobalt–ligand modes, C–S modes, near 700 cm^{-1}, appear strongly in the Raman spectra of the thiourea complexes, as shown in Figures 1 and 2. Thiourea itself has a mode at 736 cm^{-1} to which C–S stretching is the major contributor.[24] Although thiourea is conventionally described as containing a C=S double bond, this frequency is close to that expected for a C–S single bond, as observed in aliphatic thiols.[25]

$Co(TU)_2Br_2$ and $Co(TU)_2I_2$ show two ~700-cm^{-1} bands, which can be assigned to in-phase and out-of-phase stretching of the two C–S bonds. In solution both bands were found to be polarized, implying that the C–S bonds are not related by a C_2 rotation or a mirror plane, consistent with the low symmetry found in crystals.[14,22] $Co(TU)_2Cl_2$ shows only one band, the two modes evidently being coincident. This is presumably related to the accidental degeneracy of the Co–S in-phase and out-of-phase modes (245 cm^{-1}) with which the C–S stretches are coupled. On the other hand, the C–S splitting is greater for $Co(TU)_2I_2$ than $Co(TU)_2Br_2$ (30 cm^{-1} vs. 11 cm^{-1}) although the Co–S splitting is the same (13 cm^{-1}), implying a significant C–S, C–S interaction force constant for the iodide. $Co(TU)_4^{2+}$, which displays four separate Co–S modes, should likewise show four C–S modes, but only two bands are resolved.

No C–S modes could be identified in the spectra of the aminomercapto or benzenethiolate complexes, but this may be due to the poor quality of the spectra and the complexity of the ligands. For benzenethiolate, the C–S coordinate is heavily mixed with those of the ring.[25]

Resonance Enhancement Factors. Tetrahedral Co^{II} complexes display significant Raman enhancements in resonance with their visible d–d envelopes, primarily via a vibronic (*B* term[26,27]) mechanism, which favors asymmetric modes.[2,4,5] When the symmetry is lowered significantly, however, symmetric modes also gain intensity, as they become effective in mixing the transition dipoles of the coupled electronic states.[2] This pattern is also displayed by the complexes included in the present study. Thus the low-symmetry $Co(TU)_2X_2$ complexes show comparable intensities for all four cobalt–ligand stretching modes (Figure 1). In $Co(TU)_4^{2+}$, which has four equivalent sulfur ligand atoms but symmetry substantially lower than tetrahedral,[22] the breathing mode (230 cm^{-1}) is active but is appreciably weaker than the asymmetric stretching components (Figure 2).

It is of interest to estimate the magnitude of the enhancements for comparison with related systems and also to evaluate the prospects for monitoring cobalt(II)–ligand modes in proteins. For the 247-cm^{-1} peak of $Co(TU)_2Cl_2$, which probably contains both symmetric and asymmetric Co–S modes, the molar scattering factor relative to the 938-cm^{-1} (ν_1) mode of SO_4^{2-} is 12.4, with 587-nm excitation, which is at the peak of the excitation profile (see below). This value was obtained both from pellet spectra and from measurements in acetone solution. In comparison, the molar scattering factors for $Co(ImH)_2Cl_2$ (ImH = imidazole) are ~4.3 and ~8.0 for the symmetric and asymmetric Co–ImH stretch, near the visible absorption maximum.[2] The similarity in the resonance factors is reasonable, since the absorptivities of the ligand field bands of $Co(TU)_2Cl_2$ and $Co(ImH)_2Cl_2$ are also similar. In the case of $Co(SPh)_4^{2-}$, which has a lower energy charge-transfer transition (420 nm[23] vs. 320 nm for $Co(TU)_2Cl_2$[13]) the ligand field absorptivities are substantially higher, and the Raman spectrum at 647.1 nm gives a molar scattering factor for the whole Co–S envelope of ~80 relative to SO_4^{2-}.

Cobalt(II)-substituted proteins with cysteine ligands have charge-transfer bands close to that of $Co(TU)_2Cl_2$, and we anticipate comparable Raman enhancements in the visible absorption bands. Since 0.1 M SO_4^{2-} gives an acceptable reference signal, it should be possible to observe Co–S stretching modes at protein concentrations on the order of 1–10 mM.

The prospects for near-UV resonance Raman spectroscopy are inauspicious. A spectrum of $Co(TU)_2Br_2$ with 363.8-nm excitation gave a molar scattering factor for the 257-cm^{-1} Co–S band, relative to SO_4^{2-}, of only ~3.0. This is a surprisingly small value in view of the proximity of the excitation to the 320-nm S → Co charge-transfer band.[13] The C–S stretching modes, at 714 and 703 cm^{-1}, are somewhat stronger, with molar scattering factors of ~5.0. These modes are not enhanced via resonance with the visible absorption bands. Rather, their intensities decrease monotonically from the near-UV, following what appears to be an *A*-term dependence,[26,27] resonant with the 320-nm transition.

Excitation Profiles. The cobalt–ligand stretching modes of $Co(TU)_2Cl_2$ and $Co(TU)_2Br_2$ were monitored through the rhodamine 6G tunable dye laser region, which covers the high-energy end of the ligand field absorption envelopes. The resulting excitation profiles, shown in Figures 3 and 4, clearly show two maxima in a region where the absorption varies monotonically. It is not uncommon for Raman excitation profiles to display more structure than the absorption spectrum; the $Co(ImH)_2Cl_2$ profiles similarly revealed extra ligand field components.[2] The complexity of tetrahedral Co^{II} ligand field spectra is believed to reflect splittings due to spin–orbit interactions, as well as symmetry lowering and vibronic contributions.[28]

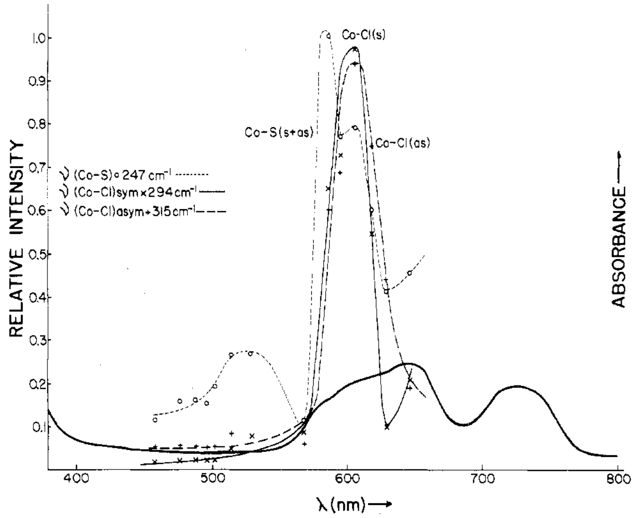

Figure 3. Excitation profiles for the metal–ligand stretching modes of $Co(TU)_2Cl_2$ in a K_2SO_4 pellet. Intensities were measured relative to that of the 983 cm^{-1} (ν_1) mode of SO_4^{2-}. The absorption spectrum (solid line) was obtained from a film evaporated on a quartz plate.

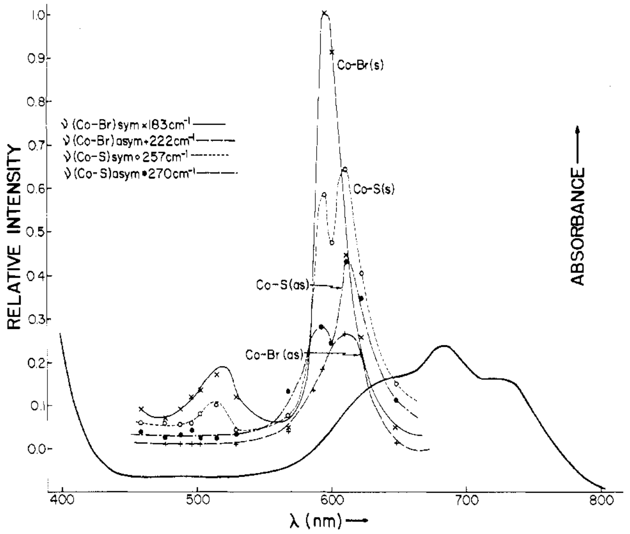

Figure 4. Excitation profiles for the metal–ligand stretching modes of $Co(TU)_2Br_2$ in a K_2SO_4 pellet. Intensities and absorption spectrum as for Figure 3.

The excitation profiles in the Ar^+ laser region showed a most unexpected feature, namely, an additional maximum at ~520 nm, observed for the 247-cm^{-1} Co–S band of $Co(TU)_2Cl_2$ and for the 183- and 257-cm^{-1} (symmetric Co–Br and Co–S) bands of $Co(TU)_2Br_2$, but not for the remaining bands. This is a region of optical transparency for both complexes, and it is not possible to attribute the peaks to an electronic resonance.

Interference phenomena can have strong influences on excitation profiles[27,29] and may manifest themselves as extra peaks and valleys. Thus centrosymmetric transition-metal complexes show excitation profile maxima well to the red of the d–d envelopes.[3] This has been attributed to interference between the weak resonance scattering from the forbidden d–d transition and the comparable preresonance scattering from higher energy charge-transfer transitions.[3] Interference of this type has been treated explicitly by Albrecht and co-workers for the forbidden $^1B_{2u}$ electronic transition of benzene.[30] Recently Ohta and Ito[31] observed a weak minimum in the Raman intensity of the 1625-cm^{-1} mode of naphthalene, well below any of the allowed transitions. They attributed the minimum to destructive interference between *B*-term scattering from the nearest excited state, and nonresonant scattering from higher states.

If two *B* terms from nearby electronic transitions interfere destructively, the off-resonance excitation profile can display

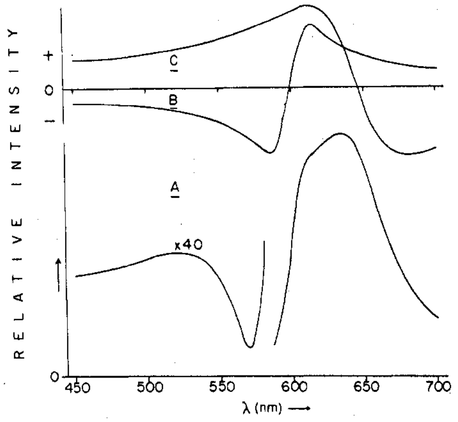

Figure 5. Calculated excitation profile (curve A) and two *B* terms[26,27] (see text): $B = M_eM_sh_{es}(\nu_s - \nu_e)^{-1}(\nu_e - \nu_0 + i\Gamma_e)^{-1}$; for B_1 (plotted as curve B) $\nu_e = 16700$ cm^{-1}, $\Gamma_e = 400$ cm^{-1}; for B_2 (plotted as curve C) $\nu_e = 15500$, $\Gamma_e = 800$ cm^{-1}. The amplitude $(M_eM_sh_{es}(\nu_s - \nu_e)^{-1})$ of B_2 is 2.45 times that of B_1, and the phases are opposite.

a trough followed by a peak. This is shown in Figure 5, where two different *B* terms, shown as curves B and C, are plotted with opposite phase. When summed and squared, they give the calculated excitation profiles shown by curve A. It exhibits the expected two (overlapping) resonance maxima but, in addition, the cited trough and peak off-resonance. This interference pattern, which depends on the detailed shape of the off-resonant *B* terms, is sensitively dependent on the *B*-term parameters, namely, the resonant energies, the bandwidths, and the relative amplitudes. In this calculation, these parameters were taken directly from the $Co(TU)_2Cl_2$ absorption spectrum (Figure 3). The absorption band near 600 nm can be deconvoluted into two components, centered at 16 700 and 15 500 cm^{-1}, with half-bandwidths 400 and 800 cm^{-1} and integrated intensities in the ratio 1:2.45. The calculated excitation profile gives an off-resonant peak which happens to fall exactly where it is observed for the 247-cm^{-1} mode of $Co(TU)_2Cl_2$. Furthermore, any significant variation of these parameters results in a washing out of the peak. This agreement is intriguing, although there is a substantial quantitative discrepancy between calculated and observed excitation profiles, since the off-resonance peak is calculated to be over 40 times weaker than the resonant peak. As seen in Figure 3, the actual off-resonance peak is only about 5 times weaker than the resonant peak. The latter may be subject to additional interferences, however, between the extra resonances that are evident in the excitation profile, which were not included in the calculation. The situation is too complex to justify a detailed analysis. At this stage the calculation represented by Figure 5 is merely to be taken as a model of how excitation profile maxima that are well removed from absorption bands can arise via fortuitous interferences.

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Registry No. $Co(TU)_2Cl_2$, 14240-49-4; $Co(TU)_2Br_2$, 14302-00-2; $Co(TU)_2I_2$, 14240-50-7; $Co(DETU)_2Cl_2$, 21307-76-6; $Co(DESU)_2Cl_2$, 68200-86-2; $Co(TU)_4(NO_3)_2$, 16774-38-2; $Co(SPh)_4(PPh_4)_2$, 57763-37-8; $Co(S\text{-}N)_2$, 61872-19-3.

References and Notes

(1) (a) Princeton University. (b) Rutgers University.
(2) S. Salama and T. G. Spiro, *J. Am. Chem. Soc.*, **100**, 1105 (1978).
(3) P. Stein, V. Miskowski, W. H. Woodruff, J. P. Griffin, K. G. Werner, B. P. Gaber, and T. G. Spiro, *J. Chem. Phys.*, **64**, 2159 (1976).
(4) Y. M. Bosworth, R. J. H. Clark, and P. C. Turtle, *J. Chem. Soc., Dalton Trans.*, 2027 (1975).
(5) G. Chottard and J. Bolard, *Chem. Phys. Lett.*, **33**, 309 (1975).
(6) B. L. Vallee and W. E. C. Wacker, "The Proteins", Vol. V, Hans Neurath, Ed., 2nd ed., Academic Press New York, 1970.
(7) J. E. Coleman, *Biochemistry*, **4**, 2644 (1965).
(8) D. R. McMillin, R. C. Rosenberg, and H. B. Gray, *Proc. Natl. Acad. Sci. U.S.A.*, **71**, 4760 (1974).
(9) C. I. Branden, H. Jornwall, H. Eklund, and B. Furngren, "The Enzymes", Vol. XI, P. D. Boyer, Ed., 3rd ed., Academic Press, New York, 1975.
(10) J. H. R. Kagi and B. L. Vallee, *J. Biol. Chem.*, **236**, 2435 (1961).
(11) D. Mastropaolo, J. A. Thich, J. A. Potenza, and H. J. Schugar, *J. Am. Chem. Soc.*; **99**, 424 (1977).
(12) D. G. Holah and D. Coucouvanis, *J. Am. Chem. Soc.*, **97**, 6917 (1975).
(13) O. Piovessana and C. Furlani, *J. Inorg. Nucl. Chem.*, **30**, 1249 (1968).
(14) W. A. Spofford, P. Boldini, E. L. Amma, P. Carfagno, and P. S. Gentile, *Chem. Commun.*, 40 (1970).
(15) F. A. Cotton, O. D. Faut, and J. T. Mague, *Inorg. Chem.*, **3**, 17 (1964).
(16) M. Bonamico, G. Desset, V. Fares, and L. Scaramuzza, *J. Chem. Soc., Dalton Trans.*, 876 (1973), and references therein.
(17) R. A. Zingaro, F. C. Bennett, Jr., and G. W. Hammar, *J. Org. Chem.*, **18**, 292 (1953).
(18) S. Rudich, T. Fawcett, and H. J. Schugar, unpublished results.
(19) D. M. Adams and J. B. Cornell, *J. Chem. Soc. A*, 884 (1967).
(20) H. G. M. Edwards, L. A. Woodward, M. J. Gall, and M. J. Ware, *Spectrochim. Acta, Part A*, **26a**, 287 (1970).
(21) J. L. Burmeister and F. Basolo, *Inorg. Chem.*, **3**, 1587 (1964).
(22) P. Domiano and A. Tiripichio, *Cryst. Struct. Commun.*, **1**, 107 (1972).
(23) D. Swenson, N. C. Baeziger, and D. Coucouvanis, *J. Am. Chem. Soc.*, submitted for publication.
(24) G. B. Aitken, J. L. Duncan, and G. P. McQuillan, *J. Chem. Soc. A*, 2695 (1971).
(25) F. R. Dollish, W. C. Fateley, and F. F. Bentley, "Characteristic Raman Frequencies of Organic Compounds", Wiley, New York, 1974.
(26) J. Tang and A. C. Albrecht, *Raman Spectrosc.*, **2**, 33–67 (1970).
(27) T. G. Spiro and P. Stein, *Annu. Rev. Phys. Chem.*, **28**, 501 (1977).
(28) C. J. Ballhausen, "Introduction to Ligand Field Theory", McGraw-Hill, New York, 1962.
(29) J. Friedman and R. M. Hochstrasser, *Chem. Phys. Lett.*, **32**, 414 (1975).
(30) G. M. Korenowski, L. D. Ziegler, and A. C. Albrecht, *J. Chem. Phys.*, **68**, 1248 (1978).
(31) N. Ohta and M. Ito, *J. Chem. Phys.*, **65**, 2907 (1976).