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Resonance Raman Spectra of α-Diimine Complexes. 3. Novel Inorganic Compounds Containing Two Chromophoric Centers

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Nine novel coordination compounds containing two chromophoric groups have been synthesized: $[Fe(\alpha\text{-diimine})_3][M(dto)_2]$ (where α-diimine = 2,2′-bipyridine, 1,10-phenanthroline, and biacetyl bis(N-methylimine); dto = dithiooxalato anion; M = Ni(II) and Pt(II)) and $Fe(bpy)_{2,3}WS_4$. The selectivity of resonance Raman effect as a function of the distance between the band maxima has been studied in the former system. If two electronic absorptions overlap, the resonance Raman spectrum is dominated by bands originating in the chromophoric group with a larger absorptivity, the bands of the other species being suppressed as expected from theory. In the case of $Fe(bpy)_2WS_4$, two polymorphs (red and brown forms) have been found. These two compounds have widely differing physical properties which can be accounted for in terms of their spin states. Several spin state marker bands have been found from the comparison of resonance Raman spectra of these two forms.

Introduction

In the two previous papers we have shown that the resonance Raman (RR) effect can be used to differentiate between vibronic and pure electronic bands in the visible region of the electromagnetic spectrum.[1,2] The present work was undertaken to investigate the RR spectra of compounds containing two or more nearby electronic bands as a function of distance between the band maxima. This research is important since recently several papers[3,4] have appeared in the literature which involve RR studies in the UV region where band overlapping may be more serious than in the visible region.

In the present paper, we have synthesized a series of novel coordination compounds containing two chromophoric groups. Because of our familiarity with the Fe(II) α-diimine cationic systems,[1,2] we chose to react these with a series of dithiooxalato complex anions ($M(dto)_2^{2-}$, M = Ni(II) and Pt(II)) and with the WS_4^{2-} anion. The visible spectra of these anions are well-known[5,6] and appeared to be compatible with those of the α-diimine cations. We have formed compounds in which the absorption maximum wavelength of the anionic complex ion falls above, below, and nearly coincidentally with that of the cationic complex ion. In the case of $Fe(bpy)_2WS_4$, we have found two polymorphs which have the same composition but strikingly different properties. Resonance Raman, electronic, and infrared spectra were recorded for all of the above compounds while for the WS_4^{2-} species, magnetic susceptibilities, X-ray powder patterns, and Mössbauer spectra have also been obtained.

Experimental Section

Preparation of Compounds. The tris(2,2′-bipyridine),[7] tris(1,10-phenanthroline),[7] and tris(biacetyl bis(N-methylimine))[8] complexes of iron(II) and the bis(dithiooxalato) complexes of nickel(II) and platinum(II)[9] were prepared according to literature methods. All products were recrystallized several times from aqueous solution. The complexes listed in Table I were prepared by mixing an aqueous solution of the appropriate α-diimine ferrous complex with an aqueous solution of the dithiooxalato complex of nickel(II) or platinum(II). Precipitates were formed immediately, isolated by filtration through a glass fritted funnel, washed several times with water, and dried over sulfuric acid. Microanalytical results and λ_{max} values are listed in Table I.

The thio salt $(NH_4)_2WS_4$ was prepared according to the literature.[10] Three different compounds of the $Fe(bpy)_nWS_4$ (n = 2 or 3) type listed in Table II were prepared. Compound G was immediately precipitated by mixing together aqueous solutions of $FeCl_2\cdot6H_2O$, 2,2′-bipyridine, and $(NH_4)_2WS_4$ in a 1:3:1 molar ratio. The product is a reddish orange solid which is slightly soluble in water. Compound H (red form) was immediately precipitated by mixing together aqueous solutions of $FeCl_2\cdot6H_2O$, 2,2′-bipyridine, and $(NH_4)_2WS_4$ in a 1:2:1 molar ratio. The precipitate was washed with water and ethanol and then dried over sulfuric acid. The product is a stable red substance which is slightly soluble in water. Compound I (brown form) was obtained by mixing pyridine solutions of anhydrous $FeCl_2$ and $(NH_4)_2WS_4$, followed by the addition of a pyridine solution of 2,2′-bipyridine. A brown compound precipitated from the resulting solution upon standing. It was washed with water and ethanol and then dried in vacuo over sulfuric acid. The compound is insoluble in water and all common organic solvents. Microanalytical results and λ_{max} values for these compound are listed in Table II.

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Table I. Analytical Data and Some Physical Properties for [Fe(α-diimine)$_3$][M(dto)$_2$] Compounds

designation	compd^a	% C		% H		λ_{max}, nm
		calcd	found	calcd	found	
A	[Fe(phen)$_3$][Pt(dto)$_2$]	46.56	46.58	2.36	2.17	525, 487, 455
B	[Fe(bpy)$_3$][Pt(dto)$_2$]	42.55	42.02	2.52	2.48	542, 492, 452, 430 sh
C	[Fe(bmi)$_3$][Pt(dto)$_2$]	31.92	31.61	4.38	4.48	582, 525 sh, 480, 448, 428 sh
D	[Fe(phen)$_3$][Ni(dto)$_2$]	53.65	53.42	2.72	2.61	527, 485 sh, 440 sh
E	[Fe(bpy)$_3$][Ni(dto)$_2$]	49.59	49.58	2.94	2.88	536, 500 sh
F	[Fe(bmi)$_3$][Ni(dto)$_2$]	38.22	38.40	5.25	5.40	580, 515 sh

^{a} phen = 1,10-phenanthroline; bpy = 2,2'-bipyridine; bmi = biacetyl bis(*N*-methylimine); dto = dithiooxalate.

Table II. Analytical Data and Some Physical Properties of Fe(bpy)$_n$WS$_4$ Complexes

designation	complex	% C		% H		% S		μ_B	λ_{max}, nm
		calcd	found	calcd	found	calcd	found		
G	[Fe(bpy)$_3$][WS$_4$]	43.08	43.18	2.89	2.85	15.33	15.45	~0	543, 503 sh, 408
H	Fe(bpy)$_2$WS$_4$	35.31	35.05	2.37	2.39	18.85	18.61	2.67	542, 505 sh, 420 sh, 405
I	Fe(bpy)$_2$WS$_4$	35.31	35.52	2.37	2.31	18.85	19.15	5.00	540 sh, 488 sh, 425, 388

Spectral Measurements. Infrared spectra of the solids were recorded as Nujol mulls and KBr pellets on a Beckman IR-12 infrared spectrophotometer. Low-temperature spectra were measured as Nujol mulls on a CsI window cooled to ~15 K by a Cryogenic Technology Model 21 closed cycle helium refrigerator.

Electronic spectra were recorded as KBr pellets on a Cary Model 14 spectrophotometer.

Resonance Raman spectra were measured in the solid state with KBr as a support. To compare relative intensities, we mixed an internal standard (K$_2$SO$_4$ or KNO$_3$) homogeneously with the sample. The rotating sample technique was used to avoid thermal decomposition. Scattered radiation (90°) was dispersed with a Spex Model 1401 double monochromator. Detection was made with a cooled RCA C31034A photomultiplier tube and a Spex DPC 2 photon-counting system. Exciting lines were provided by a Spectra-Physics Model 164 Ar-ion laser (514.5, 501.8, 496.5, 488.0, 476.5, and 457.9 nm). ^{57}Fe Mössbauer spectra were recorded on equipment previously described.[11]

Magnetic Susceptibilities. Magnetic susceptibilities in the range from 297 to 81 K were determined by the Faraday method. All the susceptibilities (χ_m) were corrected for the diamagnetism of the constituent atoms by the use of the Pascal constants.[12,13] Effective magnetic moments (μ_{eff}) were obtained from the relationship $\mu_{eff} = 2.83(\chi_m T)^{1/2}$.

X-ray Diffraction. X-ray powder diffraction patterns were recorded photographically with a Debye–Scherrer camera using a Cu Kα source in conjunction with a nickel filter. The positions of the diffraction lines were measured with a rule and converted to d spacings; intensities were estimated visually.

Results and Discussion

I. Compounds Containing Dithiooxalato Ions. The [Fe(α-diimine)$_3$][M(dto)$_2$] type compounds listed in Table I are all purely ionic species. Their electronic spectra arise from the superposition of the absorptions of individual components. In the case of [Fe(phen)$_3$][Ni(dto)$_2$], the absorption maxima of the constituent parts of the molecule coincide closely, resulting in a single broad band. On the other hand, the maxima in [Fe(phen)$_3$][Pt(dto)$_2$] are markedly shifted, resulting in a well-resolved band envelope (see Figure 1). The spectra of the remaining compounds fall between these two extremes.

Raman spectra taken from these compounds clearly demonstrate the selectivity of the RR effect. When the absorption maxima of a specific compound are well separated, the vibrational modes associated with a given electronic transition can be enhanced by irradiation with a laser energy that falls within the envelope of the electronic absorption band. This
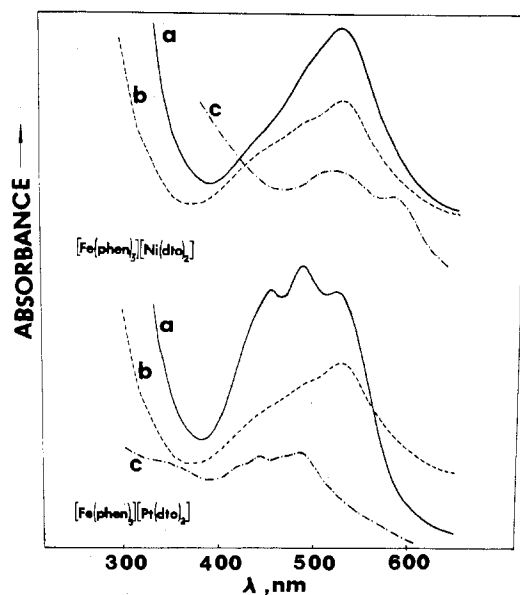

Figure 1. Electronic spectra of [Fe(phen)$_3$][M(dto)$_2$] type compounds in KBr pellets. Upper trace: (a) [Fe(phen)$_3$][Ni(dto)$_2$], (b) [Fe(phen)$_3$]Cl$_2$, and (c) K$_2$[Ni(dto)$_2$]. Lower trace: (a) [Fe(phen)$_3$][Pt(dto)$_2$], (b) [Fe(phen)$_3$]Cl$_2$, and (c) K$_2$[Pt(dto)$_2$].

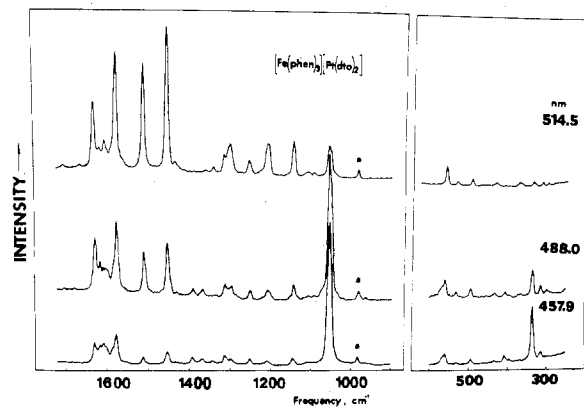**Figure 2.** Resonance Raman spectra of [Fe(phen)$_3$][Pt(dto)$_2$] in the solid state. The asterisk indicates the 984-cm^{-1} band of the internal standard (K$_2$SO$_4$).

is most vividly apparent in the spectra of [Fe(phen)$_3$][Pt(dto)$_2$] which are depicted in Figure 2. When a Raman spectrum is obtained by using the 514.5-nm line, which falls within the envelope of the Fe(phen)$_3$$^{2+}$ charge-transfer (CT) band,[14] only

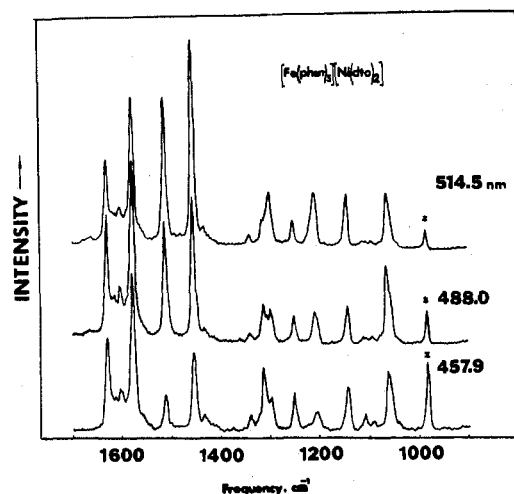(11) S. L. Ruby, B. J. Zabransky, and J. G. Stevens, *J. Chem. Phys.*, **54**, 4559 (1971).

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Figure 3. Resonance Raman spectra [Fe(phen)$_3$][Ni(dto)$_2$] in the solid state. The asterisk indicates the 984-cm^{-1} band of the internal standard (K$_2$SO$_4$).

modes associated with the ring structure of the α-diimine are enhanced. Among them, the bands at 1630, 1578, 1512, and 1454 cm^{-1} are most conspicuous.[1] On the other hand if 457.9-nm radiation is used to excite within the Pt–dto CT band, the α-diimine modes are rather weak compared with bands at 1058 and 340 cm^{-1} which are due to [ν(C–C) + ν(C–S)] and ν(Pt–S) of the Pt(dto)$_2^{2-}$ ion, respectively.[15]

If the absorption maxima of the constituents of a given compound overlap one another, the selectivity of the RR effect is lost and the Raman spectra obtained will be dominated by modes associated with the moiety giving rise to the stronger electronic transition. This effect can be seen in Figure 3, which depicts the Raman spectra of [Fe(phen)$_3$][Ni(dto)$_2$] taken at various wavelengths. We[1] have previously shown that the RR scattering intensity of the Fe(α-diimine)$_3^{2+}$ ion originates via an Albrecht "A" term, and since the RR spectrum of the Ni(dto)$_2^{2-}$ ion is dominated by polarized vibrations, we may assume that the same mechanism is in effect. The molar absorptivity of the Fe(phen)$_3^{2+}$ ion (ϵ 11.5 × 10^3) is about 3 times larger than that of the Ni(dto)$_2^{2-}$ ion (ϵ 3.7 × 10^3). Then, the relative enhancement ratio of these bands should be about 9:1. Thus, the 1063-cm^{-1} band [ν(C–C) + ν(C–S)] of the Ni(dto)$_2^{2-}$ ion is never dominant as is seen in Figure 3. In the absence of the Fe(α-diimine)$_3^{2+}$ ion, however, the Ni(dto)$_2^{2-}$ ion shows very strong Raman scattering. These results clearly show that one must be very cautious in using the relative enhancement, or lack thereof, of vibrational modes to make conclusions concerning the make-up of electronic bands. The experimental manifestation of the ϵ^2 factor in the "A" term is more pronounced than one might at first suspect.

II. Compounds Containing Tetrathiotungstate Ions. Three compounds containing the Fe(bpy)$_n$ (n = 2 or 3) and WS$_4^{2-}$ moieties were prepared as shown in Table II. While attempting to prepare Fe(bpy)$_2$WS$_4$, we found that two compounds, red (H) and brown (I), could be obtained, depending upon the method of preparation. The former was obtained from aqueous solution while the latter was produced from a pyridine solution of anhydrous starting materials. The elemental analysis of each compound corresponds quite closely to the theoretical predicted for Fe(bpy)$_2$WS$_4$ and differs significantly from those of possible structures which incorporate solvent molecules. Both compounds were analyzed for C, H, and S at two different times, giving very close agreement. The
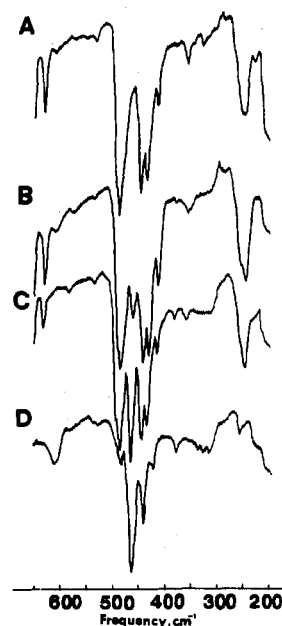

Figure 4. Infrared spectra of Fe(bpy)$_2$WS$_4$ in the region 650–200 cm^{-1} as prepared from various solvents: (A) pure pyridine; (B) 1:1 pyridine–water mixture; (C) 1:3 pyridine–water mixture; (D) pure water.
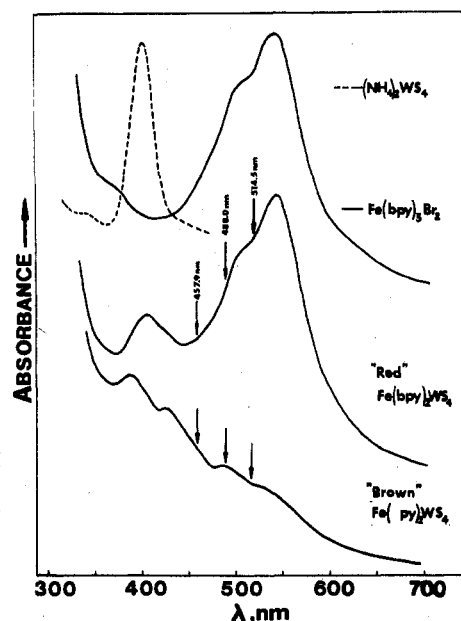

Figure 5. Electronic spectra of brown and red forms of Fe(bpy)$_2$WS$_4$ along with those of (NH$_4$)$_2$WS$_4$ and Fe(bpy)$_3$Br$_2$ in KBr pellets. Vertical arrows indicate laser wavelengths used for resonance Raman measurements.

values listed in Table II are averages of these two results. The physical properties of these two compounds are markedly different as shown below. If a mixture of pyridine and water is used as a solvent, a mixture of the red and brown compounds is obtained, the ratio being determined by the percentage of pyridine or water in the mixed solvent. This is clearly demonstrated by the infrared spectra of the Fe(bpy)$_2$WS$_4$ obtained from various mixed solvents (Figure 4). The fact that we were able to prepare one form of Fe(bpy)$_2$WS$_4$ in the presence of the other (see Figure 4B,C) is evidence for their uniqueness.

(a) X-ray Powder Patterns. Powder patterns for Fe(bpy)$_3$WS$_4$ and the red form of Fe(bpy)$_2$WS$_4$ each had strong lines corresponding to ca. d = 6.5 and 6.1 Å and were nearly identical throughout. The powder pattern of the brown form

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Table III. Magnetic Data for [Fe(bpy)$_2$WS$_4$]

					Red Form							
T, K	81.1	100.9	120.2	139.9	160.1	179.5	198.9	218.1	236.7	257.3	277.3	297.3
$10^6\chi_m$, cgsu	6844	5834	5227	4668	4306	4006	3819	3594	3482	3295	3164	2995
μ_{eff}	2.11	2.17	2.24	2.29	2.35	2.40	2.46	2.50	2.57	2.60	2.65	2.67
					Brown Form							
T, K	82.3	102.5	121.1	140.8	160.9	180.2	199.9	219.3	238.4	258.3	277.6	297.4
$10^6\chi_m$, cgsu	5418	5026	5076	5350	5962	6661	8008	9195	10053	258.3	10602	10502
μ_{eff}	1.89	2.03	2.22	2.45	2.77	3.10	3.58	4.01	4.38	4.65	4.85	5.00

was quite different and showed its strongest lines at angles corresponding to ca. $d = 8.5$ and 7.4 Å. Attempts to recrystallize and grow single crystals failed in all cases.

(b) Electronic Spectra. Figure 5 shows the electronic spectra of (NH$_4$)$_2$WS$_4$, Fe(bpy)$_3$Br$_2$, and both forms of Fe(bpy)$_2$WS$_4$. The strong band at ca. 540 nm with a shoulder at 500 nm arises from the metal–ligand CT of the Fe(bpy)$_n$ moiety.[14,16] A metal–ligand CT band also arises from the WS$_4^{2-}$ anion at ca. 400 nm.[6] Again the red form of Fe(bpy)$_2$WS$_4$ and the Fe(bpy)$_3$Br$_2$ are very similar in the Fe–α-diimine region while the brown form shows a distinctly different pattern with a drastic reduction in the relative intensity of the Fe–ligand band. As will be shown later, the brown form is a high-spin while the red form is an intermediate-spin complex at room temperature. Previous investigators[14a,17] have shown that such difference in spin states is responsible for the observed intensity behavior of the Fe–bpy CT band in these compounds. The WS$_4^{2-}$ CT band is split by 2245 cm^{-1} in the brown form and by 880 cm^{-1} in the red form although it is less evident. Such splitting has been previously observed for Ni(en)$_2$WS$_4$;[18] however, it is of greater magnitude ($\Delta\bar{\nu} = 4200$ cm^{-1}). This is not unexpected if one considers the relative affinities of Fe^{2+} and Ni^{2+} for sulfur ligands.

(c) Magnetic Moments and ^{57}Fe Mössbauer Spectra. Fe(II) complexes are known to fall into three classes on the basis of their spin states: high spin (ground state, ^{5}T$_2$) with magnetic moments between 5.5 and 4.9 μ_B[19] and isomer shifts of 1.65–1.45 mm/s,[20] low spin (ground state, ^{1}A$_1$) with near zero magnetic moments[19,21] and isomer shifts of 0.40–0.00 mm/s,[20] and intermediate spin (ground state, ^{3}T$_1$ or ^{3}T$_2$) with magnetic moments between 4.0 and 2.8 μ_B and isomer shifts comparable to those of low-spin complexes at room temperature.[19,21]

[Fe(bpy)$_3$]WS$_4$ has a magnetic moment near zero as expected for a low-spin complex and its isomer shift is 0.56 mm/s. The results of magnetic measurements of both forms of Fe(bpy)$_2$WS$_4$ in the 298–80 K range are given in Table III. These data show that the brown form is high spin at 297.4 K (5.00 μ_B) and undergoes a ^{5}T$_2 \rightarrow {}^1$A$_1$ spin conversion as the temperature is lowered. It maintains a rather large magnetic moment even at 82.3 K (1.89 μ_B), showing that the spin transition is not complete.[21] At room temperature, its Mössbauer spectrum did not show distinct peaks and the isomer shift was not observable. This result may be attributed to a small recoilless fraction of the high-spin complex.[22]

The red form has a magnetic moment of 2.67 μ_B at 297.3 K which is reduced to 2.11 μ_B at 81.1 K. A similar result is reported for Fe(mbi)$_2$(NCS)$_2$ (mbi = N,N'-bis(p-methoxyphenyl)-2,3-butanediimine) which gives a magnetic moment of 3.07 μ_B at 295 K and 2.1 μ_B at 80 K.[22] This result was interpreted in terms of a spin crossover which involves a

relatively small energy gap between the high- and low-spin states.[22] In our case, the infrared spectrum of the red form does not indicate the presence of the high-spin state in the above temperature range (vide infra). Furthermore, its susceptibilities from 297 to 81 K are approximated by the Curie–Weiss law, $\chi_m = C_m/(T - \theta)$ where θ is -70 K. Thus, it is most likely that the red form is in the intermediate spin state as are [Fe(bpy)$_2$ox] and analogous complexes.[19] The Mössbauer spectrum of the red form at room temperature exhibits two distinct peaks with an isomer shift of 0.5 mm/s, a value close to those of intermediate-spin complexes.[19]

(d) Infrared Spectra. The infrared spectrum of (NH$_4$)$_2$WS$_4$ exhibits a strong band at 458 cm^{-1} (F$_2$) with a shoulder at 484 cm^{-1} (A$_1$) of the tetrahedral WS$_4^{2-}$ ion.[23] It is apparent from Figure 4 that the symmetry of the WS$_4^{2-}$ ion has been lowered in both red (483, 463, and 441 cm^{-1}) and brown (492 (sh), 486, 443, and 432 cm^{-1}) forms of Fe(bpy)$_2$WS$_4$. The splitting of the F$_2$ mode is larger in the brown than in the red form, suggesting a stronger Fe–WS$_4$ interaction for the former. It was also noted that the spectrum of the brown form is very similar to that of the M(WS$_4$)$_2^{2-}$ ion (M = Fe(II), Zn(II), Co(II), and Ni(II)) in which the WS$_4^{2-}$ ion coordinates to the central metal (M).[23,24]

The Fe–N stretch for the brown (high spin) form is observed at 248 cm^{-1} in good agreement with other known high-spin iron(II)–α-diimine complexes.[25] This band is not observed in the spectrum of the red complex, indicating the absence of the high-spin state. Instead, it exhibits the Fe–N stretch at 379 cm^{-1} which is close to the values of low-spin complexes.[26] This is expected since König and Madeja[19] have already shown that the infrared and Mössbauer spectra of intermediate-spin complexes are similar to those of low-spin complexes. It was not possible to locate the Fe–S stretch which is expected to be weak and to be in the same area where the Fe(bpy)$_2$ moiety shows many bands.[24]

Low-temperature infrared studies of the high-spin (brown) complex showed a decrease in the intensity of the 248-cm^{-1} band with the concomitant appearance of a band at 360 cm^{-1}, indicating a high–low-spin crossover. The spectral change was reversible and kinetically slow. Along with the 360-cm^{-1} band, a new peak appeared at 457 cm^{-1}. This band is quite close to the major peak of the red form at 463 cm^{-1}. The infrared spectrum of the red form did not show any noticeable temperature dependence. This fact together with the absence of the 248-cm^{-1} band suggests that the red form does not involve the high-spin state.

The mid-infrared spectra of the two compounds were also quite distinctive and different: the spectrum of the brown form is similar to that of known high-spin complexes while the spectrum of the red form is close to that of low-spin systems.[21] For example, the former exhibits a band at 629 cm^{-1} characteristic of a high-spin complex whereas the latter does not

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(26) B. Hutchinson, J. Takemoto, and K. Nakamoto, *J. Am. Chem. Soc.*, **92**, 3335 (1970).
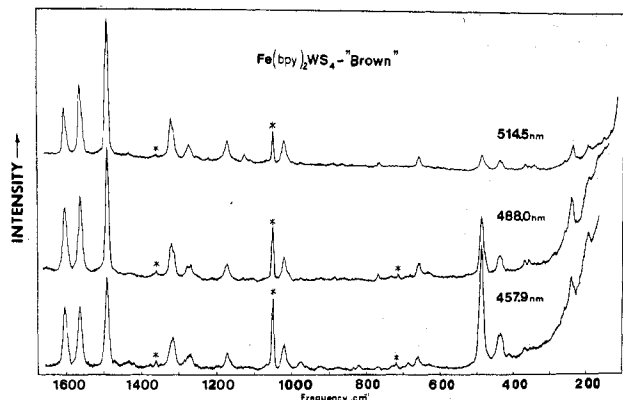
Figure 6. Resonance Raman spectra of brown $Fe(bpy)_2WS_4$ in the solid state. The asterisks indicate bands due to the internal standard (KNO_3).

give such a band. When the temperature of the brown form was lowered, the spectrum began to resemble that of a mixture of the brown (high spin) and red (intermediate spin) forms. Since the spectra of intermediate and low-spin complexes are similar,[19] this result indicates the occurrence of the high–low-spin crossover in the brown complex.

(e) Resonance Raman Spectra. Figure 6 shows the RR spectra of the brown form taken with three different exciting lines. The bands between 1600 and 600 cm^{-1} are all due to the α-diimine ligand vibrations.[1] The selectivity of the RR effect is again apparent in the fact that when 514.5-nm radiation (which falls in the region of the Fe–bpy CT transitions) is used, the spectrum is dominated by the bpy ring modes. Among them, the three bands at 1606, 1563, and 1492 cm^{-1} are most strongly enhanced.[1] Conversely when the brown compound is excited in the region of the WS_4^{2-} electronic absorption (e.g., 457.9-nm excitation), the WS_4^{2-} stretch (A_1) at 489 cm^{-1} becomes the strongest band. The F_2 mode which occurs at 446–440 cm^{-1} is not enhanced, suggesting that the resonance effect is of Albrecht "*A*" type. The Fe–N stretching mode is clearly discernible at 242 cm^{-1}. This band is absent in the RR spectrum of the red form.

The RR spectra of the red form taken at the same wavelengths as before were nearly identical with those of the brown form in the region of 1600–600 cm^{-1}. One exception is noted, however, that the 662-cm^{-1} band which is relatively weak in the brown form is much stronger in the red form. As pointed out previously, the RR spectrum of high-spin $Fe(bpy)_2Cl_2$ exhibits an anomalously weak band at 660 cm^{-1} relative to $[Fe(bpy)_3](ClO_4)_2$[1] and $[Os(bpy)_2Cl_2]^2$ (low spin). Thus this band together with the position of the Fe–N stretch can be used as spin markers. It is interesting to note that rather subtle changes are seen in the RR spectra of the brown and red forms in the 1600–600-cm^{-1} region compared with profound changes observed in infrared spectra.[26]

In the region of the WS_4^{2-} CT bands (400–440 nm), we observed that the enhancement of the red form was minimal. This can be understood by inspection of the electronic spectrum which shows that the WS_4 CT band is shifted to higher energies. Thus it was not possible to cause strong resonance with this part of the complex by using our available laser sources. The Fe–N stretch in this case occurs at 374 cm^{-1} which is close

to that observed for the $Fe(bpy)_3^{2+}$ ion (370 cm^{-1}).[1]

(f) Structural Considerations. As described above, our results on magnetic susceptibilities and Mössbauer, electronic, and infrared spectra are all compatible with the pseudooctahedral geometry of Fe(II). In fact, our data are in good agreement with those obtained for analogous $Fe(\alpha$-diimine$)_2X_2$ (X = CN^-, Cl^-, SCN^-, etc.) type compounds,[19,25,26] which are known to be pseudooctahedral. Furthermore, the electronic and vibrational spectra of both forms of $Fe(bpy)_2WS_4$ show that the WS_4^{2-} ion tends to coordinate to Fe(II) rather than to remain as a free ion. On the basis of these findings, we consider the probable structures of these two compounds.

First, the possibility of cis–trans isomerism[27] seems unlikely in view of the severe steric hindrance of the 3 and 3′ protons of bpy.[28,29] Insolubility of these compounds in common solvents suggests that they are polymeric. Thus polymeric structures in which the *cis*-$Fe(bpy)_2$ units are bridged via the WS_2 group are most probable.

Although the exact structures of these two forms are not known, it is most likely that they have basically the same geometrical arrangement, only the coordinate bond lengths around the metal being different due to the difference in spin states. It is well-known that complexes such as $Fe(bpy)_2$-$(NCS)_2$ are high spin at room temperature and low spin at 100 K and that their coordinate bond lengths[30] and infrared spectra[25,31] are markedly different between these two spin states. Our results described above are similar to the high- and low-spin $Fe(bpy)_2(NCS)_2$ except that we were able to isolate two spin isomers at room temperature.

Finally, it is interesting to compare the magnitude of the Fe–bpy and Fe–WS_4 interactions for these two spin states. In the red form, we observed the Fe–N stretch at 379 cm^{-1} (IR) which is much higher than that of the brown form (high spin, 248 cm^{-1} (IR)). This indicates that the Fe–N(bpy) interaction is stronger in the red than in the brown form. On the other hand, the Fe–S(WS_4) interaction is probably stronger in the brown than in the red form since the WS_4^{2-} CT band near 400 nm and the WS_4^{2-} group vibrations near 450 cm^{-1} give more splitting in the former than in the latter.

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