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Infrared and Raman Spectra of Bis(imidotetraphenyldithiodiphosphino-S,S') Complexes with Cu(II), Co(II) and Fe(II)

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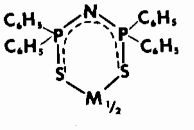
The infrared and Raman spectra of KL, FeL_2, CoL_2 and CuL_2 (L = imidotetraphenyldithiodiphosphino anion) have been obtained in the range from 1600–200 cm^{-1}. To assign the chelate ring vibrations of CuL_2, resonance Raman spectra have been measured as a function of the exciting frequency. The CuS stretching vibration (F_2) of the tetrahedral CuS_4 core has been located at 292–283 cm^{-1} based on the ^{63}Cu–^{65}Cu isotope shift observed in the far-infrared spectra. The totally symmetric CuS stretching vibration (A_1) appears strongly at 206 cm^{-1} in the Raman spectrum. These results have been utilized to assign the spectra of the remaining compounds.

Introduction

Recently, resonance Raman(RR) spectra of blue copper proteins have been studied extensively [1–4]. These investigations have shown that their Cu–S stretching vibrations at *ca.* 280–260 cm^{-1} are unexpectedly weak even when the exciting laser frequency is tuned in the Cu–S charge-transfer(CT) band near 600 nm. This anomaly was attributed to the small σ(S)–dσ(Cu) overlap by Siiman *et al.* [2] and to the indirect resonance enhancement by a UV transition by Ferris *et al.* [3]. In order to further confirm these vibrational assignments, we have studied the infrared (IR) and Raman (or RR) spectra of bis(imidotetraphenyldithiodiphosphino-S,S') copper(II) and its Co(II) and Fe(II) analogs [5].



Abbreviated as ML_2

All these compounds are known to have the tetrahedral MS_4 core. For this reason, the CuS_4 skeleton of CuL_2 is regarded as a model of the metal binding site of blue copper proteins [5].

Experimental

Preparation of Compounds

The compounds, KL, FeL_2, CoL_2 and CuL_2 were prepared according to the literature methods [5–8]. $^{63}CuL_2$ and $^{65}CuL_2$ were prepared from ^{63}CuO and ^{65}CuO, respectively, which were purchased from Oak Ridge National Laboratory. The purity of these isotopes was over 98% for ^{63}Cu and over 90% for ^{65}Cu.

Spectral Measurements

The infrared spectra of all the compounds were measured as Nujol mulls (450–200 cm^{-1}) and KBr pellets (1700–350 cm^{-1}) on a Beckman IR-12 infrared spectrophotometer. The far-infrared spectra of $^{63}CuL_2$ and $^{65}CuL_2$ were measured as Nujol mulls on a Nicolet FTIR-7199 spectrometer. The Raman spectra of KL, FeL_2 and CoL_2 were measured as KBr pellets with the 488.0 nm excitation (laser power, ~150 mw) using the rotating sample technique. The resonance Raman spectra of CuL_2 were measured at low temperatures (~20 K) by attaching the KBr pellet on a cold tip cooled by a Cryogenic Technology Model 21 cryocooler. All Raman spectra were recorded on a Spex Model 1401 double monochromator. Detection was made with a cooled RCA C31034A photomultiplier tube in the DC amplification mode. Excitations at 457.9, 488.0 and 514.5 were made by a Spectra-Physics Model 164 Ar-ion laser, and those at 578.2 and 618.2 nm were made by a Spectra-Physics Model 365 dye-laser (Rhodamine 6G) pumped by the above Ar-ion laser.

Results and Discussion

Figure 1 shows the IR spectra of KL, FeL_2, CoL_2 and CuL_2 in the 1600–400 cm^{-1} region. Previously, Schmidpeter and Groeger [6] reported the IR spectrum and band assignments of KL. However, no IR or Raman spectal data were available for its metal complexes. In this work we have obtained the IR and

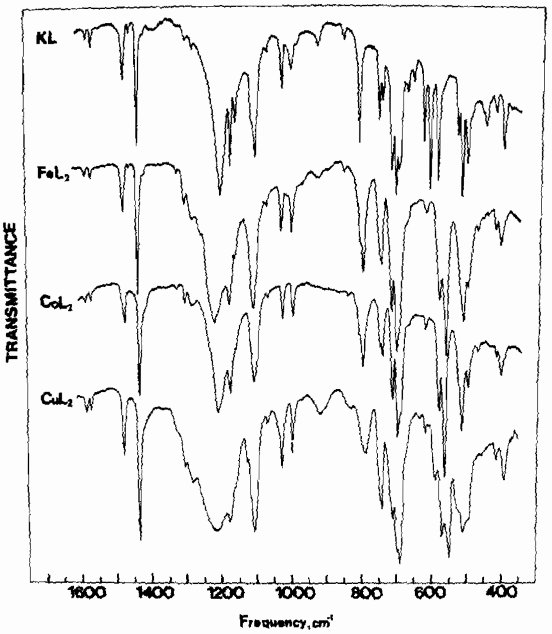


Fig. 1. Infrared spectra of KL, FeL_2, CoL_2 and CuL_2 in the 1600–400 cm^{-1} region.

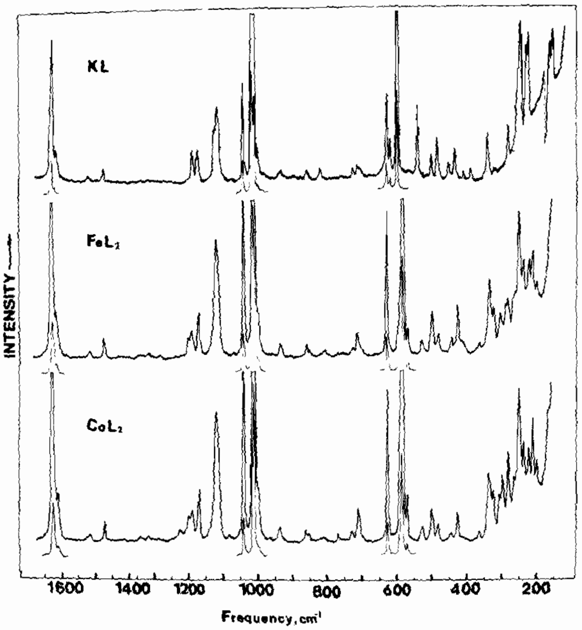


Fig. 2. Raman spectra of KL, FeL_2 and CoL_2 in the 1700–200 cm^{-1} region (excitation, 488.0 nm; power, ~150 mw; resolution, 1 cm^{-1}).

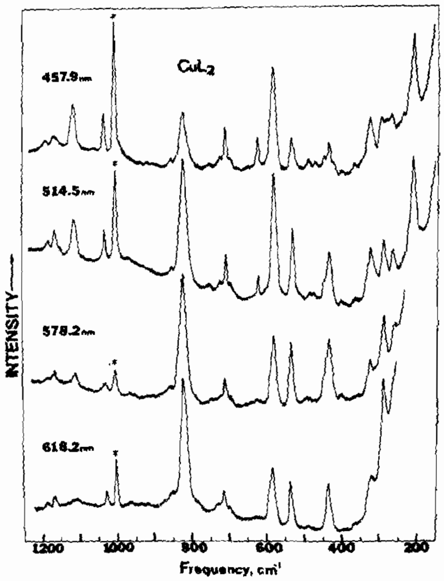


Fig. 3. Resonance Raman spectra of CuL_2 at various exciting wavelengths. The asterisks indicate the 1002 cm^{-1} line of the phenyl vibration (internal standard).

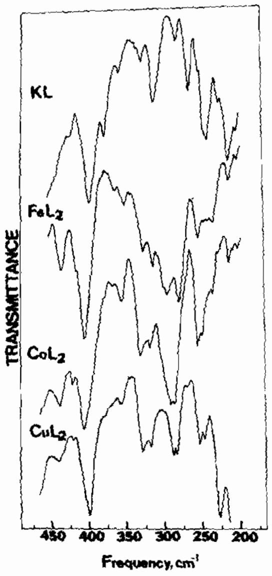


Fig. 4. Far-infrared spectra of KL, FeL_2, CoL_2 and CuL_2 in the 450 to 200 cm^{-1} region.

Raman spectra of all these compounds (Figs. 2–4). According to the theory of resonance scattering [9], the intensities of the chelate ring vibrations should be enhanced when the exciting laser frequency approaches that of the metal–chelate ring (L) charge-transfer(CT) transition. In the case of CuL_2, such a transition is known to be at 575 nm [5]. Thus the intensities of all the vibrations involving the PN, PS and CuS bonds are expected to be maximized as the energy of the exciting laser beam is matched to that of the Cu–L CT transition. As stated before, the MS vibrations are of our particular interest. To locate CuS stretching vibrations, we have prepared $^{63}CuL_2$ and $^{65}CuL_2$, and measured their isotope shifts in the far-IR region.

TABLE I. Vibrational Frequencies (cm^{-1}) and Band Assignments.

K^+L^-		FeL_2		CoL_2		CuL_2		Assignment
IR	Raman	IR	Raman	IR	Raman	IR	Raman	
1199vs		1221vs, br	1193w, sh	1215s, br	1218vw	1217s, br	1220vw, sh	
1187sh	1180w			1193sh	1194sh			ν_a(PNP)***
1173s	1172n, sh	1178s	1186w	1176s	1184w	1178s	1178vw	
808s	815vw	808sh	800w	810w, sh	808vw	–	818vs*	ν_s(PNP)
715s	717vw	716s	718w, sh	715s	719vw	715s	720vw, sh	
703vs	705w	702s	708vw	703vw	706w	703s	708w	ν(PC)
696s	698vw	698sh	697w, sh	694s	696vw, sh	692vs	694w, sh	
586s	588vs	582m	574vs	580m	576vs	593m	580s*	ν_s(PS)
608s	610vw	563s	562w	566s	565vw	572s	–	
						553s		ν_a(PS)
528m	529m	529w, sh	521w	523w, sh	522w	528w, sh	530ms*	δ(PNP)
426w	428w	419w	421w	421w	422w	423m	427m*	δ(NPS)
–	–	297w, sh	298vw	300w, sh	303w, sh	301sh	297w, sh	
–	–	280m	283w	292m	292w	292w (1.5)**	284*	ν(MS), F_2
				288m		283w (1.5)**		
267w	273w	–	276w	275w, sh	276w	–	277w, sh	
259w, sh	258w, sh	255w	256w, sh	256w	256w, sh	258w	268w	
243w	240ms	242w, sh	244ms	246w, sh	244ms	247w, sh	245vw, sh	
227w, sh	223m	233w, sh	231w	234w, sh	232w	230	228w, sh	***
215w	217ms	216w	217m	215w	216w	–	215w, sh	
–	–	–	205ms	–	207ms	–	206*	ν(MS), A_1
–	154ms	–	–	–	–			
	147m							

ν, stretching; δ, bending; vs, very strong; s, strong; ms, moderately strong; m, medium; w, weak; vw, very weak; sh, shoulder; br, broad. *Strongly enhanced by resonance. **Isotope shift due to the ^{63}Cu–^{65}Cu substitution. ***Phenyl vibrations may be hidden or overlapped.

Table I lists the IR and Raman frequencies and band assignments for KL, FeL_2, CoL_2 and CuL_2. Most of the phenyl vibrations were identified based on the well-known group frequencies of monosubstituted benzenes [10], and deleted from Table I for the sake of simplicity. However, some phenyl vibrations may be overlapped by other modes, as indicated in the table.

The $P \overset{\dots}{-} N \overset{\dots}{-} P$ stretching frequencies are known to be 1210–1190 cm^{-1} for cyclic $[NP(C_6H_5)_2]_{3,4}$ [11]. Since the PN bond orders of the present compounds are similar to the above compounds, we have assigned the strong IR bands near 1200 cm^{-1} to ν_a(PNP). The location of the corresponding symmetric mode, ν_s(PNP), is not clear in the Raman spectra of KL, FeL_2 and CoL_2 shown in Fig. 2. However, Fig. 3 shows that the 818 cm^{-1} band of CuL_2 is strongly enhanced when the exciting laser wavelength is close to 575 nm where the Cu–L CT band is located [5]. Thus, this band of CuL_2 and similar weak bands near 800 cm^{-1} of other complexes have been assigned to ν_s(PNP).

The P–C stretching frequencies are in the range from 780–620 cm^{-1} [12]. Thus, the three IR bands at *ca.* 700 cm^{-1} of all the compounds have been assigned to the ν(PC) of various symmetry types. The corresponding Raman bands are generally weak (Fig. 2). Even in the case of CuL_2, these modes are not resonance-enhanced since the P–C bonds do not belong to the metal–chelate ring system (Fig. 3).

The $P \overset{\dots}{-} S$ stretching vibrations of metal diphenyldithiophosphinato complexes are reported to be in the range of 590–530 cm^{-1} [13, 14]. As is seen in Fig. 3, CuL_2 exhibits a band at 580 cm^{-1} which is strongly enhanced by the 578.2 excitation. This band has been assigned to ν_s(PS). Two strong IR bands at 572 and 553 cm^{-1} of CuL_2 are close to the 580 cm^{-1} Raman band and assigned to ν_a(PS).

In addition to the 818 cm^{-1} band, CuL_2 exhibits several bands which are strongly enhanced when the exciting frequency approaches the energy of the Cu–L CT transition. They are at 530, 427, 284 and 206 cm^{-1}. The most likely assignments for the first two bands are the PNP and NPS bending modes, respectively. This is based on the assumption that the XYZ angle bending frequency is roughly given by the equation: 1/4 [ν(X–Y) + ν(Y–Z)] [15]. Then, δ(PNP) and δ(NPS) are estimated to be about 500 and 450 cm^{-1}, respectively.

Figure 4 shows the far-IR spectra of the four compounds in the 450–200 cm^{-1} region where the MS stretching vibrations are expected. We have found that the 292 and 283 cm^{-1} bands of CuL_2 are shifted by *ca.* 1.5 cm^{-1} by the ^{63}Cu–^{65}Cu substitution. These bands can be assigned to the Cu–S stretching band (F_2) of the tetrahedral CuS_4 core which is probably split by the solid state effect. Similar bands are observed for CoL_2 at 292 and 288 cm^{-1}, and for FeL_2 at 280 cm^{-1}. As expected, KL itself does not exhibit such bands.

As seen in Fig. 3, CuL_2 exhibits a strong band at 206 cm^{-1} when excited by the 457.9 and 514.5 nm lines. Unfortunately, we were unable to observe this band by the 578.2 nm excitation because of the broad and steep background by the Rayleigh line. We assign this band to the A_1 type CuS_4 stretching mode since it is extremely strong even at off-resonance. The frequency of 206 cm^{-1} is lower than those reported previously for blue copper proteins (300–250 cm^{-1}) [1–4]. However, this may be attributed to the differences in structure (tetrahedral CuS_4 core *vs.* pseudo tetrahedral CuN_2SX or trigonal bipyramidal CuN_4S core (X = N, S or O)) [4] and/or in the M–S bond order (ionized *vs.* neutral sulfur).

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