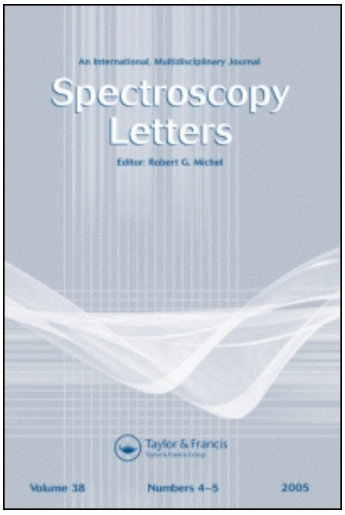

Spectroscopy Letters
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597299

Infrared Spectra of Morfolonium $(mpH)_2Mo_2Cl_6(H_20)_2$(I),$(mpH)_2Mo_2Cl_xBr_{6-x}(H_2O)_2$(II)/ $(mpH)_2Mo_2Br_6(H_2O)_2$(III) and the Pyridinium $(PyH)_2Mo_2I_6(H_2O)_2$(IV)Hexahalo-di(aquo): dimolybdate(II) Complexes, Containing Quadruple Metal-Metal Bounds

V. K. Ceylan[a]
[a] Afyon Kocatepe Üniversitesi, UŞLAK, TÜRKIYE

To cite this Article Ceylan, V. K.(1996) 'Infrared Spectra of Morfolonium $(mpH)_2Mo_2Cl_6(H_20)_2$(I),$(mpH)_2Mo_2Cl_xBr_{6-x}(H_2O)_2$(II)/ $(mpH)_2Mo_2Br_6(H_2O)_2$(III) and the Pyridinium $(PyH)_2Mo_2I_6(H_2O)_2$(IV)Hexahalo-di(aquo): dimolybdate(II) Complexes, Containing Quadruple Metal-Metal Bounds', Spectroscopy Letters, 29: 8, 1555 — 1561
To link to this Article: DOI: 10.1080/00387019608007146
URL: http://dx.doi.org/10.1080/00387019608007146

SPECTROSCOPY LETTERS, 29(8), 1555-1561 (1996)

INFRARED SPECTRA OF MORFOLONIUM $(mpH)_2Mo_2Cl_6(H_2O)_2$(I),$(mpH)_2Mo_2Cl_xBr_{6-x}(H_2O)_2$(II), $(mpH)_2Mo_2Br_6(H_2O)_2$(III) AND THE PYRIDINIUM $(PyH)_2Mo_2I_6(H_2O)_2$(IV)HEXAHALO-DI(AQUO) DIMOLYBDATE(II) COMPLEXES, CONTAINING QUADRUPLE METAL-METAL BOUNDS

Key words: Infrared spectra; Ionic interactions; Morpholinium and the Pyridinium Hexahalo-di(aquo) dimolybdate(II) complexes, with quadruple molybdenum-molybdenum bonds.

V.K. Ceylan

(Afyon Kocatepe Üniversitesi, Mühendislik Fakültesi, UŞAK -TÜRKIYE)

ABSTRACT

The electronic (800-400 nm), infrared (4000-200,400-20 cm^{-1}), ordinary Raman (400-200 cm^{-1}) spectra of morpholinium and the pyridium hexahalo-di(aquo) dimolybdate(II) complexes, containing quadruple metal-metal bonds were investigated. The electronic spectra of the solid compounds at various temperatures (25,100 and 300K) demonstrate intense and structured bands in the visible region (510-582 nm) attributed to the expected $\delta \rightarrow \delta^*$ transitions.

From the infrared and Raman spectra, the skeletal stretching modes in these complexes have been localized, and the charecteristic bands of these ions were observed in the expected regions.

Finally, the ionic interections were relatively weak, but the existance of phenomena was perceptible and the result was obtained in agreement with X-ray data.

INTRODUCTION

Over the past decade, a wide variety of quadruple metal-metal bonded complexes have been synthesized (1). Much of the interest has focused on the structural properties of these and related species were investigated by the method of X-ray crystallography(2,3) and infrared (4), Raman (5), resonance Raman (6) spectrescopy.

In this context, several hexahalo-di (aquo) dimolybdate (II) anions, $Mo_2X_6(H_2O)_2^{2-}$, containing quadruply bonded molybdenum atoms have been prepared and characterized by X-ray diffraction methods (7-8). $Mo_2X_6(H_2O)_2^{2-}$ seems to be the most frequently found halodimolybdate group in the presence of pyridinium ($C_5H_5NH^+$ or pyH^+), of 4-methylpyridinium ($CH_3C_5H_4NH^+$ or $picH^+$) and of morpholinium ($C_4H_8ONH_2^+$ or mpH^+) countercations. These anions generally contain a short metal-metal quadruple bond (ca $2.12A^0$) and water molecules are coordinated to molybdenum at ca $2.20\ A^0$, so that anions possess a centre of symmetry and an overall symmetry near to C_{2h} and the cations possess an overall symmetry near to C_{2v}.

The spectroscopic studies have been performed (9-12) detailly on the above complexes. The aim of this work was to investigate the ionic interections phenomena and to inform the obtained vibrational wavenumbers and the assignements of infrared (4000-200 cm^{-1}) spectra of these complexes.

EXPERIMENTAL

Preparative details

A gift from J.V. Brencic, the morpholinium salts $(mpH)_2Mo_2Cl_6(H_2O)_2$(I), $(mpH)_2Mo_2Cl_xBr_{6-x}(H_2O)_2$ (II),$(mpH)_2Mo_2Br_6(H_2O)_2$(III) and the pyridinium complex $(pyH)_2Mo_2I_6(H_2O)_2$(IV) were prapared by the methods given in the literature(7,8).

All compounds except II were recsystallized from 1:1 mixtures of halide acids and of the appropriate morpholinium or pyridinium salt. The recrystalizations of II from a 1:1 Hbr gave III.

Instrumental details

Electronic spectra were recorded using a Cary 17 spectrometer either in the diffuse reflectance mode (at 300K) or in the transmission mode with potassium or caesium halide pressed discs at various temperatures (25-300K).

The low-temperature spectra were obtained using a liquid nitrogen cryostat or a Cryodine Model 21 closed-cycle helium refrigerator. Infrared spectra of the complexes were recorded from nujol or fluorolube mulls held at 300K or at ca 80K by use of Perkin- Elmer 225 and 180 spectrometers (400-180 cm^{-1}) and of a Polytec FIR 30 interferometer (250-20 cm^{-1}).

Raman spectra were recorded with either a Coderg T800 or a Dilor RT130 triple monochromator instrument using nine emission lines of Model 164 Spectra-Physics Kr^+ and Ar^+ lasers (λ_0 from 676.4 to 457.9 nm). Dedection was by conventional d.c. techniques using a cooled RCA C31034 photomultiplier tube.

Repeat scan measurements were carried out with a Mostek Z80 microprocessor and all data could also be transferred to a PDP 11 computer. Spectra

from samples held at room temperature were obtanined by use of a sample holder rotating at ca 1600 rev min^{-1} (13,14) and those from samples held at ca 25-80K were obtained from K_2SO_4 or $KClO_4$ sample discs in conjuction with a glass block rotating at ca 1500 rev min^{-1}; the latter refracts the incident laser beam across the surface of the sample in order to minimize any local heating effects.

RESULTS

Electronic spectra

The electronic spectra of I, II, III, and IV at 300K in the transmission or diffuse reflectance mode exhibit intense broad bands at about 515, 520, 534 and 582 nm, respectively.

These bands were confidently assigned(9,10)to the $^1Ag \rightarrow {}^1Au$ or $\delta(a_g) \rightarrow \delta^*(a_u)$ (in the C_{2h} symmetry group) axially polarized and dipole allowed transitions by anology with the corresponding transitions in similar $Mo_2X_8^{4-}$, $Mo_2(SO_4)_4^{4-}$ or $Mo_2X_4L_4$ systems with qadruple Mo-Mo bonds (11).

Infrared and ordinary Raman spectra

Structure and selection rules.

Compound IV crystallizes in the monoclinic space group $P2_1/c$ (or C^5_{2h}) and the unit cell contains four cations on general positions and two anions on C_i sites (7).

One can assume isomorphous structures for the morpholinium complexes even though X-ray results (8) prove that they crystallize in the triclinic $P\bar{1}$ space group with anions located on symmetry centres.

To a first approximation, the symmetry of an isolated pyridinium, (py H^+) cation belongs to the C_{2v} point group and the 30 internal vibrations can be classified:

$$\Gamma^{C2v}_{vib}=11A_1 (R,IR)+3A_2 (R)+6B_1 (R,IR)+10B_2 (R,IR)$$

All the modes are active in Raman spectra and 27 vibrations are active in infrared spectra. The morpholinium (mpH^+) cation was considered the same symmetry C_{2v} and its internal vibrations:

$$\Gamma^{2v}_{vib}=13A_1 (R,IR)+8A_2 (R)+9B_1 (R,IR)+12B_2 (R,IR)$$

All the modes are active in Raman spectra and 34 vibrations are active infrared spectra.

Vibrational results

The structure of an isolated $Mo_2X_6(H_2O)_2^{2-}$ anion, belongs to the C_{2h} point group and the internal vibrations infrared and Raman spectra (λ_0=647.1 nm) were registred in the 20-400 cm^{-1} range where all the fundamental vibrations of the binuclear anions were expected.

Some typical spectra, the corresponding band wavenumbers, and the proposed assignements were reported(9,10).

Internal vibrations of the cations were considered in this article, therefore, a complete list of the infrared wavenumbers (4000-200cm^{-1}), assignements based on those known for morpholine (15) and various pyridinium salts (16) were reported in table 1. The infrared spectra of the 4 complexes were illustrated in Fig. 1.

TABLE 1. Vibrational wavenumber (cm^{-1}) *and assignments of infrared spectra of complexes (I,II,III,IV)*

$(mpH)_2Mo_2Cl_4(H_2O)_2$	Assignments	$(mpH)_2Mo_2Cl_2Br_{2-x}(H_2O)_2$	Assignments	$(mpH)_2Mo_2Br_4(H_2O)_2$	Assignments	$(pvH)_2Mo_2I_4(H_2O)_2$	Assignments
3495 vw	$\nu(OH_2)$	3480 w	$\nu(OH_2)$	3371 w	$\nu(OH_2)$	3540 sh	$\nu(OH_2)$
3361 m		3365 m		3295 sh		3410 ml	
3248 m	$\nu_s(NH_2)$ or	3250 m	$\nu_s(NH_2)$ or	3251 m	$\nu_s(NH_2)$ or	3352 s	combination
3133 m	$\nu_s(NH_2)$	3126 m	$\nu_s(NH_2)$	3125 m	$\nu_s(NH_2)$	3236 w	
3046 m		3040 m		3040 m		3208 m	
3012 vw		3006 vw		3005 vw		3151 m	
2993 vw		2990 sh	$\nu_a(CH_2)$or	2991 vw	$\nu_a(CH_2)$0r	3124 w	ν(CH)
2975 vw	$\nu_a(CH_2)$ or	2961 w	$\nu_a(CH_2)$	2962 w	$\nu_a(CH_2)$	3096 m	
2967 w	$\nu_s(CH_2)$	2868 w		2868 w		3067 sh	
2870 w		1625 w	$\delta(OH_2)$	1624 w	$\delta(OH_2)$	3060 ms	ν(NH)
1635 w	$\delta(OH_2)$	1568 s	$\delta(NH_2)$	1569 sh		3032 vw	
1576 s	$\delta(NH_2)$	1560 sh		1564 s	$\delta(NH_2)$	2968 w	
1570 sh		1466 vw		1560 sh		2952 w	
1467 sh		1455 sh		1466 w		2916 w	combination
1457 sh		1448 m	$\delta(CH_2)$	1452 sh		2900 w	
1450 m	$\delta(CH_2)$	1439 m		1448 m	$\delta(CH_2)$	2844 w	
1441 m		1420 vw					
1424 w		1405 m					
1406 m		1395 m		1439 m		1636 sh	
1395 m		1387 w		1437 sh		1631 ms	$\delta(OH_2)$
1389 m		1377 m	twist(CH_2)	1419 w		1608 w	
1377 m	twist(CH_2)	1344 m		1404 m		1600 vs	
1343 m		1313 sh		1395 m		1577 s	
1315 sh		1305 m		1387 w		1569 sh	
1306 m		1283 w		1377 w	twist(CH_2)	1534 sh	
1288 m		1216 w	wag(CH_2)	1343 w		1532 vs	skeleton
1217 m	wag(CH_2)	1184 m		1313 sh		1527 sh	
1185 m		1168 w		1305 m		1517 sh	
1180 sh		1092 vs	ν(cycle)	1289 w		1483 vs	
1170 w		1085 sh		1223 sh	wag(CH_2)	1479 sh	
1092 vw	ν(cycle)			1216 w		1473 sh	
1070 sh				1184 w			
1037 m	rock(CH_2)	1036 ms	rock(CH_2)	1179 vw		1377 s	
1027 m		1026 m		1167 vw		1363 ml	
1017 m		1016 w		1098 sh		1324 m	δ(CH)
982 m		874 m		1092 vs	ν(cycle)	1257 w	
976 sh	ν(cycle)	867 vs	ν(cycle)	1085 sh		1245 w	δ(NH)
869 vs				1035 m	rock(CH_3)	1236 m	
865 sh				1026 w		1195 m	
839 sh				1016 w		1186 sh	
819 m	rock(CH_2)	816 w	rock(CH_2)	874 m	ν(cycle)	1160 w	δ(CH)
772 w				867 vs		1060 w	
588 m		585 m		863 sh		1051 m	
486 w				815 w	rock(CH_2)	1026 vs	skeleton
474 w	δ(cycle)	472 vw	δ(cycle)	584 m		1005 w	
448 sh				470 vw		993 w	
440 m		438 m		438 m	δ(cycle)	991 w	γ(CH)
415 m		414 m		412 m		928 wl	γ(NH)
395 m	ν(Mo-O)	385 w	ν(Mo-O)	378 w	δ(Mo-O)	896 w	
375 sh						873 vs	
374 vs	ν(Mo-Cl)	300 ml	ν(Mo-Cl)			856 vs	
		276 vw				791 w	
273w				255vw		740ms	γ (CH)
266w		256w		245vw		730vs	
255w						672sh	
						666vs	
						635w	
						608w	skeleton
						520ml	
						386w	ν(MoO)
						287wl	
237wl	δ(MoMoO)	237w	δ(MoMoO)	239m	ν(Mo-Br)	245w	δ(MoMoO)
228sh							
220m		219m	ν(MoBr)	219m		215sh	
208m	δ(MoMoO)	207w	δ(MoMoO)	206m	δ(MoMoO)	207ms	δ(MoMoO)

w:Weak: m: Medium: s: Strong: l: Large: v: Very: sh: Shoulder

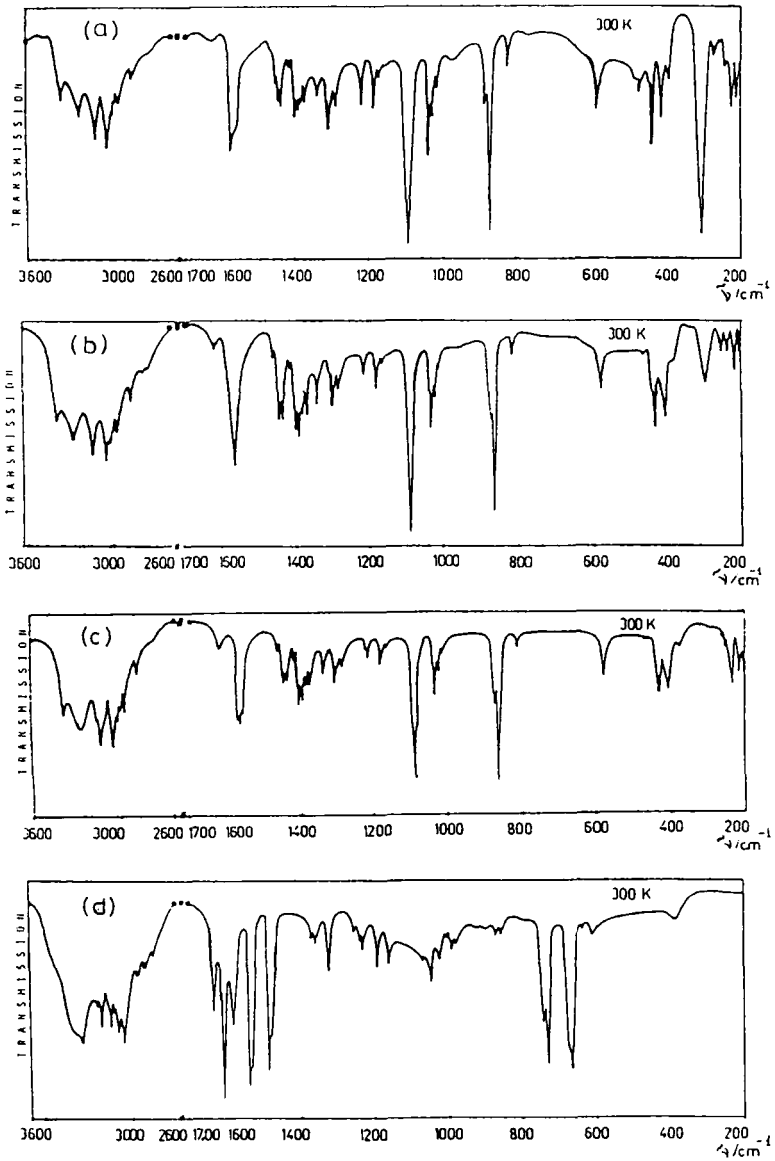

Fig. 1 Infrared spectra of (a) $(mpH)_2Mo_2Cl_6(H_2O)_2$ (b) $(mpH)_2 Mo_2Cl_xBr_{6-x}(H_2O)_2$, (c) $(mpH)_2 Mo_2Br_6(H_2O)_2$ and (d)$(pyH)_2Mo_2I_6(H_2O)_2$ in the 4000-200cm^{-1} wavenumber range.

DISCUSSION

The characteristic bands of these cations (mpH^+,pyH^+) were observed in the expected regions. This result is in good agreement with previous studies (15,16). The case, we were interested in the ionic interctions of these complexes. Totally symmetric Raman stretching vibration $\tilde{\nu}$(Mo-Mo) of quadruple molybdenum-molybdenum bonds is in a linear variation with the mass which is including molybdenum and its ligands (12).The wavenumber $\tilde{\nu}$(Mo-Mo) varies as a function of ligands (X) and as a function of the cations (mpH^+, pyH^+) as well.

Since $\tilde{\nu}$(Mo-Mo) was determined as $\tilde{\nu}=AM_X+B$ then the data of three complexes (I,II,III) were fitted on the line, but, the complex (IV) has a different cation, pyridinium (pyH^+) and its coordinates were slightly off the line. This cation made different effect on the anion [Mo_2X_6 $(H_2O)_2^{2-}$] in comparison with morpholinium (mpH^+) cation. In conclusion, the ionic interections of these complexes were relatively weak, but the axistance of phenomena was perceptible and the result was obtained in good agreement with X-ray data.

REFERENCES

1) F.A. Cotton, Chem. Soc. Rev. 1975; 4:27
2) J.V. Brencic and F.A. Cotton, Inorg. Chem. 1969; 8:2698
3) J.V. Brencic and F.A.Cotton, Inorg Chem. 1970; 9:346
4) C. Oldham and A.P. Ketteringham, J. Chem. Soc., Dalton Trans. 1973; 2304
5) J. San Fillipo and H.J. Sniadoch, Inorg. Chem. 1973; 12:2326
6) R.J.H. Clark and M.L. Franks,J.Am.Chem. Soc. 1976;98:2763
7) J.V.Brencic and P.Segedin, "The structures and the preparation of Hexahalo-di (aquo) dimolybdedate (II) Anions." Inorg Chim.Acta 1978; 29:281
8) J.V.Brencic, L.Golic and P.Segedin, "The structures and the preparations of Hexahalo-di (aquo) dimolybdedate (II) Anions."Inorg.Chim. Acta 1982; 57:247
9) V.K.Ceylan "Etute experimantale et théorique des spectres électroniques et Raman de résonance de composés à liasions quadruples Mo≡Mo" These 3e cycle, Univ.Paris 6 1983.
10) V.K.Ceylan, C.Sourissean and J.V.Brencic, "Electronic, Infrared, Raman and Resonance Raman Spectra of some Hexahalo-di(aquo) dimolybdate(II) Anions, $Mo_2X_6(H_2O)_2^{2-}$, with Quadruple Molybdenum-Molyndenum Bonds" J.R. Spectroscopy 1985;16:128
11)V.K.Ceylan, "EXPERIMENTAL AND THEORETICAL STUDY OF "ANOMALOUS"-INTENSITY VARIATIONS IN THE RESONANCE RAMAN EXCITATION PROFILES OF THE FUNDEMENTAL AND ITS OVERTONES FOR TOTALLY SYMMETRIC RAMAN STRETCHING VIBRATION $\tilde{\nu}$(Mo-Mo) OF QUADRUPLE MOLYBDENUM -MOLYBDENUM BONDS" Spectroscopy Letters 1995;28:8
12)V.K.Ceylan, "Totally symmetric Raman Stretching Vibration $\tilde{\nu}$(Mo-Mo) of Quadruple Molybdenum - Molybdenum Bonds, is In a Linear Variation with the mass which is including Molybdenum and its Ligands" 1996 (Under press)
13) R.J.H.Clark, "In advances in Infrared and Raman Spectroscopy." edited by R.J.H.Clark and R.E.Hester. Heydon ,London 1977; 1:143

14) W.Kiefer, "In advances in Infrared and Raman Spectroscopy." edited by R.J.H. Clark and R.E.Hester.Heydon, London 1977, 3:1
15) P. V. Shanbhag, M.A. Shashidham and K.S. Rao, "Infrared Spectra of Morpholine." Indian J. Phys. 1979;53B:140
16) R. Foglizzo and A.Novak, "Infrared Spectra of Prydinium Salts" J. Chim Phys. 1969;66:1539.

Received: May 1, 1996
Accepted: June 10, 1996