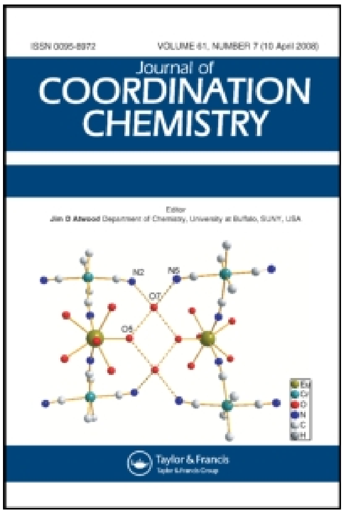

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

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To cite this Article Prados, Ronald A. , Clausen III, Chris. A. and Good, Mary L.(1973) 'A MÖSSBAUER STUDY OF A SERIES OF RUTHENIUM(II) PENTAAMINES', Journal of Coordination Chemistry, 2: 3, 201 — 205

To link to this Article: DOI: 10.1080/00958977308072972

URL: http://dx.doi.org/10.1080/00958977308072972

J. Coord. Chem., 1973, Vol. 2, pp. 201–205

A MÖSSBAUER STUDY OF A SERIES OF RUTHENIUM(II) PENTAAMINES[1]

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(*Received January* 31, 1972; *in final form July* 11, 1972)

The Mössbauer spectra of a series of ruthenium(II) pentaammines were obtained at 4.2°K. The trends in isomer shift and quadrupole splitting parameters can be related to the relative delocalization of the ruthenium t_{2g} electrons ("back bonding") by the ligand X in the complexes, $[Ru(NH_3)_5X]^{+n}$. The delocalization associated with the CO ligand is shown to be significantly greater than that for the N_2 ligand in this series of complexes.

INTRODUCTION

The synthesis of hexaammineruthenium(II) chloride by Lever and Powell[3] in 1959 and later by Allen and Senoff[4] through a different method, opened several new synthetic pathways to the preparation of many ruthenium(II) pentaammine complexes. The only Ru(II) pentaammines known prior to 1959 were $[Ru(NH_3)_5NO]Cl_3 \cdot H_2O$ and $[Ru(NH_3)_5SO_2]Cl_2$, which had been synthesized and reported in the old German literature.[5,6] The most noteworthy of the recent pentaammine ruthenium(II) complexes was the novel molecular nitrogen adduct which was isolated by Allen and Senoff.[7] This complex was one of the first reported molecular N_2 compounds and was extensively investigated. The stability of the complex was attributed to the ability of the N_2 ligand to "back bond" with the filled t_{2g} orbitals on the metal. The isoelectric pentaammine carbonyl complex was prepared almost simultaneously by Allen, *et. al.*[8] and Stanko and Starishak.[9] On the basis of spectroscopic evidence the latter authors stated that the "back bonding" ability of the N_2 ligand was equal to or greater than that of the carbonyl. The Mössbauer effect has been shown to be a useful tool in the evaluation of "back bonding" in ruthenium(II) pentacyano complexes[10] and in low spin iron(II) complexes.[11] Since other complexes of the pentaammine series could be prepared, i.e. the pyridine, the benzonitrile, the nitrosyl, etc., a Mössbauer study of this series appeared to be an effective mechanism for determing the position of N_2 as a "back bonding" ligand.

EXPERIMENTAL

The Mössbauer spectra were obtained on powdered absorbers with both the source and absorber maintained at 4.2°K. The source which was prepared by New England Nuclear Corp., Boston, Massachusetts, consisted of approximately 5 mCi of 16 day Rh^{99} in a host lattice of ruthenium metal. The cryogenic and electronic apparatus have been described elsewhere.[12,13] All absorbers contained a natural abundance of Ru^{99}. Because of the small effect observed for these compounds, most runs were continued until the count rate per channel exceded 2×10^6. The experimental Mössbauer data were fitted through a least squares method to Lorentzian line shapes and then plotted on a line printer or a Houston Instruments' plotter using a DEC–PDP–10 computer. Typical spectra are shown in Figure 1.

The complexes were prepared by previously published methods and authenticated by metal analysis and infrared spectroscopy. Metal analyses were generally obtained by hydrogen reduction of the complexes to ruthenium metal in a hydrogen stream at 600°C. In the case of the two perchlorate salts of the nitrile complexes this analytical method was not feasible since the materials exploded at elevated temperatures. A spectrophotometric method developed by Banks and O'Laughlin[14] using 1, 10-phenanthroline as a complexing reagent was substituted. In all cases the % Ru found was with ±0.1% of the calculated value.

Infrared spectra were run on a Perkin–Elmer Model 357 and/or FIS–3 spectrophotometer and compared to the reported literature values. Preparative literature references are indicated in Table I.

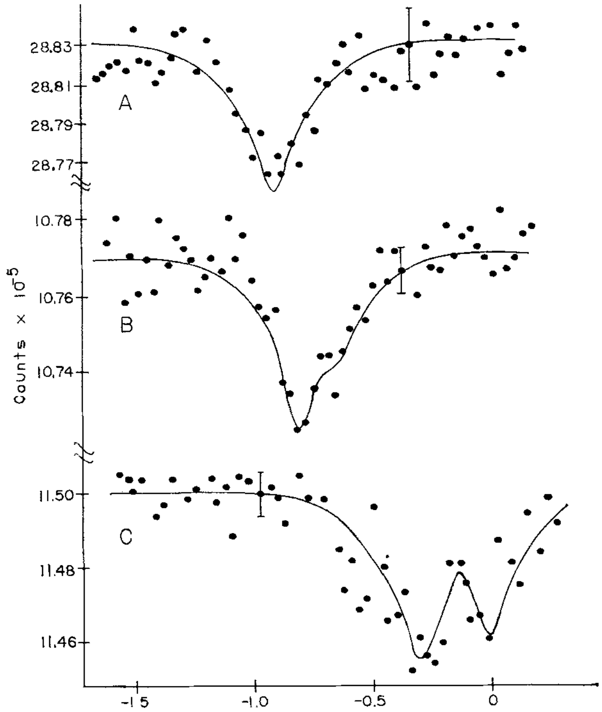

FIGURE 1 Representative Mössbauer Spectra for Ru (II) Pentaammines.

A. $[Ru(NH_3)_6]Cl_2$
B. $[Ru(NH_3)_5N_2]Cl_2$
C. $[Ru(NH_3)_5NO]Cl_3 \cdot H_2O$

RESULTS AND DISCUSSION

The Mössbauer parameters of the ruthenium(II) pentaammines are given in Table I. Note that there is good agreement between the values reported here and those of other workers for the three complexes, $[Ru(NH_3)_6]^{++}$, $[Ru(NH_3)_5N_2]^{++}$, and $[Ru(NH_3)_5NO]^{+++}$. This type of cross-check is important in systems like ruthenium where little Mössbauer data is available and where low percentage absorption values are prevalent. The isomer shifts in the series of pentaammines show a definite decrease in going through the series:

$$NO^+ \gg CO > SO_2 > N_2 \sim pz > CH_3CN \sim C_6H_5CN > en > py \sim NH_3$$

Since the nuclear factor, $\Delta R/R$ for Ru^{99} is positive, a decrease in isomer shift implies a decrease in the s-electron density about the ruthenium nucleus.[21,22] The isomer shift can be related to the σ-bonding and π-delocalizing ability of the ligands involved[23] and for the pentaammines could be written as:

$$\text{I.S.} \propto \sigma_{NH_3} + \pi_{NH_3} + \sigma_X + \pi_X.$$

For these complexes, σ_{NH_3} for the five NH_3 ligands should be essentially constant and π_{NH_3} should be negligible. Thus the variation observed is due to some combination of σ_X and π_X where π_X represents the delocalization of the filled t_{2g} ruthenium electrons into ligand orbitals of appropriate energy and symmetry. Unfortunately, there may be a "synergic" effect between σ_X and π_X and it will be difficult to separate the individual contributions of each. However, for other complexes of this type and for several low-spin iron(II) complexes, evidence has been presented which indicates that the contribution from π_X is more important than that from σ_x.[20,23] This concept is borne out by the quadrupole splitting data discussed below. The effect of this ($M \rightarrow L$) π-bonding would be seen as an increase in the isomer shift since the s-electron density would increase because of the decreased d-electron shielding. The parameters in Table I indicate that this trend is realized as the isomer shift increases in the pentaammines as the sixth ligand is changed from NH_3 to NO^+. This series of pentaammines provides an ideal model for comparing this "back bonding" ability of ligands. Ammonia is capable of σ-bond formation only, having no available orbitals for forming ($M \rightarrow L$) π-bonds. Figgis and co-workers[24] have shown that delocalization into NH_3 from the $t_{2g}{}^6$ set in Ru(II) complexes is negligible. Thus the extent of $t_{2g}{}^6$ delocalization into other ligands can be qualitatively expressed by comparing an affected parameter with what is found for the NH_3 ligand. For example, the isomer shift of the hexaammine complex can be assumed to represent a case of Ru(II) with no increase in metal s-electron density due to "back bonding." An observation of the value for the NO^+ complex indicates that it has increased into the range expected for Ru(IV) species in an environment where no d-electron delocalization is occurring.[12,22] Thus the NO^+ entity must strongly participate in a ($M \rightarrow L$) π-bond.[10] The stability of the Ru–NO^+ bond has long been known and, in fact, much of the chemistry of ruthenium deals with this linkage.

The isomer shift of the carbonyl complex is in the upper range found for Ru(III) compounds

TABLE 1

Mössbauer parameters of the ruthenium(II) pentaammines at 4.2°K

Compound	I.S.[a,b] (mm/sec)	ΔE_q[b] (mm/sec)	Γ[c] (mm/sec)	density (mg Ru/cm^2)	Preparative Reference
$[Ru(NH_3)_6]Cl_2$	−0.91	—	0.30	260	3
	—0.92	—	0.26	—	[d]
$[Ru(NH_3)_5py](BF_4)_2$	−0.89	—	0.31	197	[e]
$[Ru(en)_3]Br_2$	−0.85	—	0.28	200	15
$[Ru(NH_3)_5C_6H_5CN](ClO_4)_2$	−0.82	—	0.26	255	16
$[Ru(NH_3)_5CH_3CN](ClO_4)_2$	−0.82	—	0.34	180	16
$[(Ru(NH_3)_5)_2pz](C_7H_7SO_3)_4$	−0.75	—	0.40	120	[f]
$[Ru(NH_3)_5N_2]Cl_2$	−0.76	0.20	0.22	143	17
$[Ru(NH_3)_5N_2]Br_2$	−0.80	0.26	0.28	—	[d]
$[Ru(NH_3)_5SO_2]Cl_2$	−0.61	0.30	0.35	96	18
$[Ru(NH_3)_5CO]Br_2$	—0.54	—	0.39	151	8
$[Ru(NH_3)_5NO]Cl_3 \cdot H_2O$	−0.16	0.34	0.31	142	3
	−0.19	0.39	0.28	—	[d]
	−0.20	0.36	0.56	—	[g]

[a] Relative to ruthenium metal.

[b] Precision is ±0.02 mm/sec.

[c] Linewidth at half-height, precision is ±0.05 mm/sec.

[d] Data taken from Ref. 19.

[e] Compound supplied by Dr. J. D. Petersen and Dr. P. Ford, University of California, Santa Barbara.

[f] Compound supplied by Dr. C. Cruetz, Georgetown University, Washington, D.C.

[g] Data taken from Ref. 20.

containing no π-bonding ligands.[19] This electron delocalization capability of the carbonyl entity is well known because of its ability to force low oxidation states in many transition metal carbonyl complexes. A comparison of the data reported here for the pentaammines with ligand X = NO^+, CO and NH_3 with the corresponding low-spin iron(II) pentacyano complexes[25] is shown in Figure 2. The essentially linear relationship which is obtained indicates that the relative effect of the ligand X on the s-electron density at the metal nucleus is the same for both low spin iron(II) $[t_{2g}{}^6e_g{}^0]$ and ruthenium(II) $[t_{2g}{}^6e_g{}^0]$ regardless of the nature of the other five ligands.

Following NO^+ and CO in the "back bonding" series shown in Table I are SO_2, pyrazine and N_2, in that order. The significant delocalization of metal d electrons into the SO_2 orbitals is not unexpected in view of the previously reported infrared data and the extremely short Ru(II)-S bond distance in the analogous complex, $[Ru(NH_3)_4SO_2Cl]Cl$.[18] The indicated electron delocalization into the pyrazine ligand is consistent with the idea that fast electronic exchange may occur between the two Ru(II) atoms via the pyrazine bridge.[26]

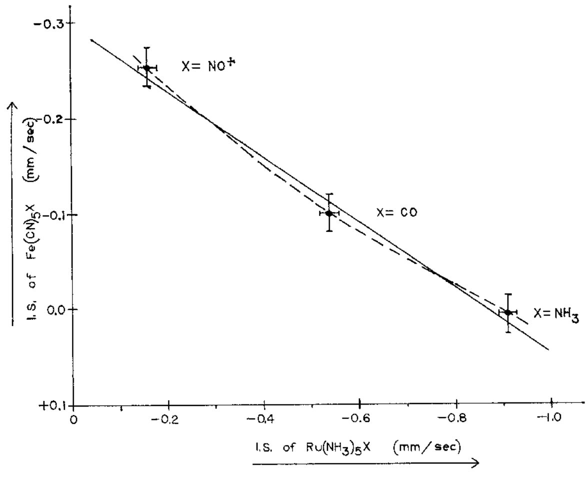

FIGURE 2 Relationship between I.S. Values for $[Fe(CN)_5X]^{-n}$ and $[Ru(NH_3)_5X]^{+n}$.

The large isomer shift difference (0.22 mm/sec) between the CO complex and the N_2 complex indicates that the "back bonding" ability of the N_2 ligand is significantly less than that exhibited by the CO ligand. A similar conclusion has been reached by Bancroft and co-workers[27] based on their Mössbauer data for an analogous set of low spin iron(II) complexes. The relationship shown in Figure 2 would imply that N_2 should exhibit the same relative effect in ruthenium as is observed. These results are in conflict with a report by Stanko and Starinshak[9] who based their conclusions on the diatomic ligand stretching frequencies of the Ru(II) complexes. However, recent molecular orbital calculations have indicated that the infrared stretching of the ligand may not reflect the d-electron delocalization into the ligand orbitals.[28] Another theoretical study concludes that the N_2 ligand would undergo a weaker interaction with the metal than CO in the complexes, $Cr(CO)_6$ and $Cr(N_2)_6$.[29] A recent investigation of the infrared *intensities* of the N_2 and CO stretching vibrations in the $Os(N_2)X_2[PR_2C_6H_5]_3$ and $Os(CO)X_2[PR_2C_6H_5]_3$ complexes supports the conclusion that the CO moiety is a more effective electron delocalizing ligand than N_2.[30] Thus it appears that the infrared, Mössbauer and molecular orbital evidence are all in agreement with respect to the relative "back bonding" ability of the CO and N_2. However, the increase in the ruthenium isomer shift of the $[Ru(NH_3)_5N_2]^{++}$ complex with respect to the hexaammine species (0.15 mm/sec) is indicative of the considerable delocalization caused by the N_2 ligand and accounts for the stability of the N_2 complex.

The isomer shifts for the two nitrile complexes indicate that the delocalization is not influenced by the nature of the organic group attached to the nitrile linkage. However, the increase in isomer shift of approximately 0.1 mm/sec from the hexaammine does indicate a significant "back bonding" capability for these ligands as predicted by Clarke and Ford[16] from infrared and U.V. spectral data. The last two ligands, pyridine and ethylenediammine appear to be behaving essentially as σ-donors in this series of Ru(II) complexes. The trend from the hexaammine to ethylenediammine is indicative of the relative positions of NH_3 and ethylenediammine in the spectrochemical series. In primarily σ-bonded complexes, the *s*-electron contribution will be more significant than *d* and *p* electron shielding effects.[31] Thus the stronger ethylenediammine ligand should cause an increase in the isomer as is observed.

The second Mössbauer parameter reported in Table I is the quadrupole splitting which reflects the magnitude of the electric field gradient (EFG) at the ruthenium nucleus. Ru(II) has a ground electronic configuration of $t_{2g}{}^6e_g{}^0$; the six paired electrons in the t_{2g} set possess cubic symmetry and should make no contribution to the valence part of the EFG. However, a lowering of symmetry due to the asymmetric expansion of the t_{2g} electrons towards the X ligand in $Ru(NH_3)_5X^{n+}$ should cause a lattice induced EFG at the ruthenium nucleus and result in the appearance of a quadrupole split spectrum.[32] If the σ_X contribution increases at the same time, this would tend to cancel the effect of the π_X contribution.[20,23] Thus the values of ΔE_q given in Table I can be adequately rationalized in terms of increased "back bonding" from N_2 to SO_2 to NO^+. The pyrazine and carbonyl complexes both have broad lines indicative of unresolved quadruple splitting. The absence of a resolved ΔE_q in the carbonyl complex may be due to the fact that this ligand is both a good σ-donor *and* π-acceptor[30]; thus the asymmetry due to the π-delocalization will be balanced by the asymmetry due to the increased σ-donation of the CO with respect to the other NH_3 ligands.[20,23]

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