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ATOMIC ENERGY COMMISSION

RECOIL CHEMISTRY AND SOLID STATE
EXCHANGE IN COBALT COMPLEXES : A NEW MODEL

by

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BOMBAY, INDIA

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INIS Subject Category : B13, B14

DESCRIPTORS

COBALT COMPLEXES

IRRADIATION

RECOILS

ISOTOPIC EXCHANGE

SOLIDS

DISSOCIATION

ANNEALING

RADIATION EFFECTS

CHEMICAL REACTIONS

ABSTRACT

During the last thirty years considerable work has been done on various aspects of recoil chemistry and solid state exchange in cobalt complexes. Several interesting features such as 'oxygen effect', 'water of hydration effect', 'dilution with isomorphous materials', etc., have been observed. These data led workers to reject the older hypothesis based on 'fragmentation' and 'recombination' and suggest models based on exciton or electron induced exchange. However some recent data shows that perhaps both the processes viz. , thermal annealing in n-irradiated systems and solid state exchange are not bulk processes. This has led the author to propose a new model. In this model greater emphasis is placed on dissociation reactions followed by recombination and / or exchange reactions.

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EXCHANGE IN COBALT COMPLEXES : A NEW MODEL

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INTRODUCTION

During the last thirty years extensive work has been done on various aspects of recoil chemistry of several complexes and oxyanions, with cobalt complexes receiving maximum attention. (1 to 5)

Though these two types of systems exhibit several parallels in behaviour, some of the more interesting features have been observed with cobalt complexes. These include 'classification into two categories viz., 'open (or sandwiched) and octahedral', 'oxygen effect', 'water of hydration effect', 'dilution with isomorphous matrices' (Refs. 2 to 4 give an exhaustive account of these).

These features led the Indian School to reject the several models formulated to explain the behaviour of oxyanions. Thus the 'hot zone model', 'cavity complex and interstitial vacancy model' etc., were found inadequate, the main criticism being that fragmentation and recombination could not take place so efficiently.

Around 1965-1968 an important breakthrough was made viz., the existence of isotopic exchange in the solid state between the parent complex and radiotracer metal (this phenomenon is also referred to as transfer annealing) in several oxyanions and cobalt complexes was demonstrated. (6 to 8) Though there is no quantitative

correlation between the two processes, there is overall qualitative agreement. This analogy led several workers to postulate new models and in almost all these models electrons or excitations induce exchange between entities.

However, a close scrutiny of observations reveal that both 'thermal annealing of reactor irradiated complexes' and 'transfer annealing in radiotracer doped complexes' (hereinafter these two processes would be referred to as 'annealing' and 'exchange') are basically processes in which the entire complex need not take part and that the processes are confined to 10^{-4} to 10^{-6} moles of the complex (in fact exchange is basically a surface reaction). This is borne by the following observations :

- (i) in reactor irradiation of a complex only a small part of the complex ($\sim 10^{-5}$ moles or even less) gets activated and one follows the chemistry of 'such hot atoms'; whether the same behaviour is followed by the bulk complex is open to question.
- (ii) in the study of exchange (9) between $^{57}\text{Co}^{2+}$ and $\text{Co}(\text{dipyridyl})_2(\text{ClO}_4)_2 \cdot 3\text{H}_2\text{O}$ exchange was observed with a $^{57}\text{Co}^{2+}$ to complex mole ratio of 2×10^{-3} ; however no exchange was observed when this mole ratio was increased to 0.2 by further diluting with unlabelled Co^{2+} .
- (iii) Sen Gupta (10) has studied exchange in $^{57}\text{Co}^{2+}$ doped $\text{Co}(\text{dipyridyl})_2(\text{ClO}_4)_2 \cdot 3\text{H}_2\text{O}$ in the presence of ions like Fe^{3+} , Fe^{2+} , Co^{4+} , Co^{3+} ; he observed that as long as the concentration of added ions is $\sim 10^{-3}\%$ of the complex, exchange is comparable whereas when the added ion concentration is increased to $10^{-1}\%$, exchange is considerably diminished (the values falling from 80% to 10%).
- (iv) in all exchange studies the extent of exchange depends on the specific activity of the dopant radiotracer.
- (v) the best support for exchange being a surface reaction, however, comes from a recent paper by Eugene Le May et al (11)

Earlier the author⁽¹²⁾ had shown that when $^{60}\text{Co}^{2+}$ is doped in $\text{Fe}(\text{Ox})_3$, the rate of exchange is very fast as seen by taking Mossbauer patterns. However, Eugene de May et al have shown that when this experiment is repeated in bulk by heating $\text{CoCl}_2 + \text{Fe}(\text{Ox})_3$, there is no transfer annealing.

Thus the author agrees with Eugene Le Mays' remarks that "it is obvious that though several authors claim large percentages of exchange in 'annealing' and 'exchange' it is always in terms of the trace amount of radio tracer present; this means that the amount of complex that undergoes exchange or annealing is really small."

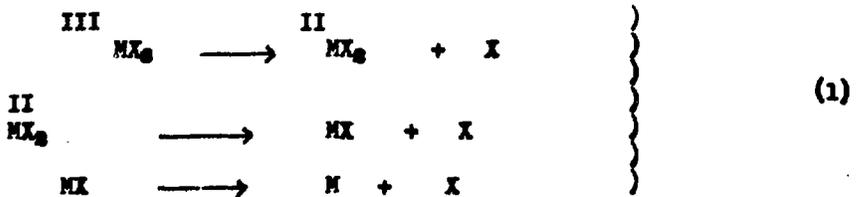
Further from the similarity of results⁽¹³⁾ obtained in both (n,γ) and (γ,n) irradiation of cobalt complexes it is apparent that irradiation as such may play only a secondary role so that the primary processes are different. Similarly the large similarities observed between thermal annealing in neutron irradiated systems and radiotracer doped exchange indicates that the same mechanism is operative in both processes; this in turn means that the irradiated complex behaves similar to the non irradiated complex as per as annealing is concerned. This makes it clear that radiation plays only a secondary role and that the primary role must come from somewhere else.

The above reasoning makes it clear that 'invoking fragmentation due to irradiation' is not relevant. Similarly the models of Amar Nath⁽⁴⁾ or Venkateswarlu⁽²⁾ where excitons or electrons are supposed to play a part and contribute to exchange reactions also do not answer the above basic questions. The present model attempts to explain the data in a new way.

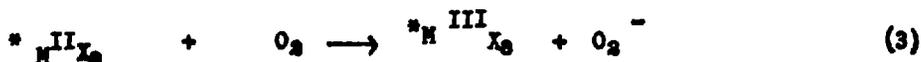
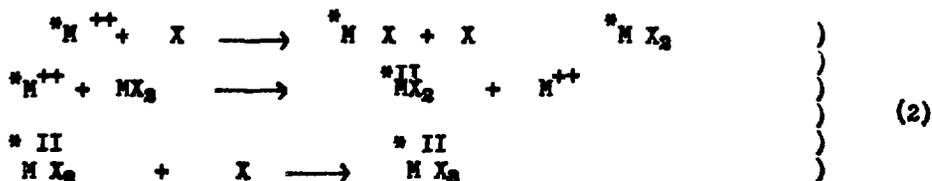
The Model

In the present model 'dissociation of the complex' is the first step followed by reformation of the parent from the dissociated entities. The first step of dissociation is depicted in equations (1) and leads to stepwise loss of ligand entities. This reaction occurs to the extent of $\sim 10^{-4}$ to 10^{-6} moles and being an equilibrium reaction can proceed in both ways.*

In the next step of combination reactions either a ligand will react with M^{++} or there could be an exchange between M^{++} and MX_2 leading to formation of MX_2 and subsequently MX_3 . These set of reactions are depicted in equations (2). The final step would be an oxidation of any $II^* MX_3$ formed to $III^* MX_3$.



* It is understood that we are referring to temperatures that are far below actual temperatures at which complete decomposition occurs.



Unfortunately rates of degradation or decomposition of complex and mode of decomposition are not well known. But from limited data it is clear that such processes do take place. Thus appreciable degradation of cobaltic acetyl acetonate ($< 0.1\%$) occurs at moderate temperatures and the degraded species appears as CO^{++} after dissolution and ion exchange separation⁽¹⁴⁾. This means that cobaltic acetyl acetonate degrades to cobaltous acetyl acetonate (which subsequently appears as CO^{++}). Similarly uranyl acetyl acetonate⁽¹⁵⁾ loses 1.5 moles of acetylacetonate at $120^\circ C$ and the process is reversible. The decomposition of hexamine metal complexes has been well studied and they follow the reaction⁽¹⁷⁾.



Such dissociation reactions would be accelerated by traces of free ligand present or other degraded species. Thus even so called thermally stable complexes like cobaltic acetylacetonate have traces of degraded species (~ 10 ppm) even after purification which multiply on thermal treatment.

We will now explain the various features based on this model. However we want to emphasize clearly that this model will explain only the qualitative features and we are not making predictions regarding quantitative results.

Interpretation of observations

(1) Differences in 'Exchange' and 'Annealing' in the same complex

It is generally seen that for the same complex the initial retention and extent of annealing are both larger as compared to initial exchange and extent of exchange (Table 1). This is to be expected since during irradiation heat is generated so that some degradation reactions might already have been initiated and further reactor irradiation makes a substance prone to easier degradation.

A direct proof of this is seen when $\text{Co}(\text{ACAC})_3$ is irradiated at -78°C ; an R_0 value of $\sim 1.5\%$ is obtained.

(2) Different extents of annealing and exchange in different complexes

According to the present model, the dissociation reaction is the one of major consequence and the extent of dissociation will naturally be different for different complexes depending on thermodynamic properties. Unfortunately not much data is available in the solid state to make predictions. However as a first approximation, the bond dissociation energies could be taken as an indication of extent of decomposition.

The best example of this can be seen in a comparison of annealing and exchange in a series of complexes derived from the same ligand. Table II lists the D_{M-0} values for metal acetyl acetonates and one can see that the order of decomposition lies in the order $Mn(ACAC)_3 > Fe(ACAC)_3 > Co(ACAC)_3 > Cr(ACAC)_3$. Thus in the exchange reaction ${}^{60}Co + M(ACAC)_3 \longrightarrow {}^{60}Co(ACAC)_3$ exchange should be in the order $Mn(ACAC)_3 > Fe(ACAC)_3 > Co(ACAC)_3 > Cr(ACAC)_3$. This is precisely what is observed ^{21,22}.

Similarly under identical irradiation conditions, $Co(ACAC)_3$ shows larger annealing than $Cr(ACAC)_3$ ⁽²¹⁾. An extension of this can be seen in diluted systems, viz., $Co(ACAC)_3 + M(ACAC)_3$ where $M = Mn, Fe, Cr$ and $Co : M$ ratio = 1 : 100 . It is seen that when these diluted systems are irradiated ⁽²²⁾, the initial retention is large and extent of annealing is fastest for the system $Co(ACAC)_3 : Mn(ACAC)_3$.

The broad classification of cobalt complexes into two categories viz., open or sandwiched and octahedral can also be understood on the above lines. The so called sandwich complexes such as vitamin B 12, cobalt phthalocyanine) show no annealing or exchange due to their inherent stability to thermal degradation.

(3) Effect of Added Ions

As pointed out earlier ⁽²⁰⁾, when extraneous ions are added in small concentrations ($\sim 10^{-5}$ moles) they do not alter the exchange or annealing but at larger concentrations ($\sim 10^{-1}$ moles) both exchange and annealing are reduced. This can be understood on the basis of competition for the ligands between the dopant ions and inactive ions;

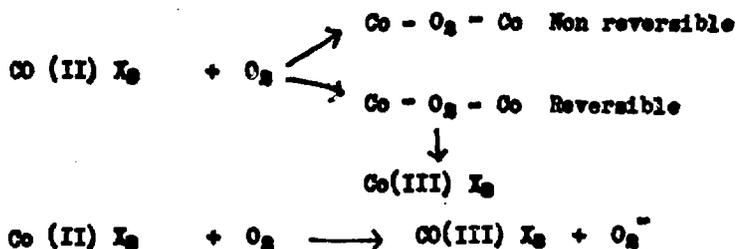
when the concentrations of both are of same order then exchange is not inhibited but when the added ion's concentration is larger than its reaction with ligand becomes more predominant. The observation on exchange being dependent on specific activity of radio tracer can also be explained on the same basis.

(4) Dual Role of Oxygen

Work with several systems in presence of oxygen and other ambients has thrown up a lot of contradictory data. Thus in some complexes oxygen is found to accelerate exchange and annealing while for others it is found to retard both annealing and exchange

The dual role of oxygen can be understood on the basis that these transition metal complexes can take up oxygen to form oxygen carriers. This idea was first mooted by Venkateswarlu^{5,26} and used by him to explain the contradictory observations. An excellent review on oxygenation is given by Erakine and Field⁽²⁵⁾ and the particular relevance to cobalt is given by Venkateswarlu⁽²⁾. Here we will only give some slight modifications of Venkateswarlu's treatment.

In general the Co (II) complexes could form both reversible and non reversible adducts and such processes will compete with oxidation reactions (equation 3 in our model)



There are three possibilities :

- (i) the complex may not form oxygen carriers (or oxidation reaction could be faster) in which case oxygen will promote annealing e.g., Na Co EDTA
- (ii) the complex may form a reversible oxygen carrier, in such cases heating at higher temperatures will result in decomposition of the adduct to cobaltic complex. In such cases one will get temperature dependent R_{α} values if annealing is done in air while R_{α} values will converge to a single but higher value if annealing is done in vacuum e.g., Co(ACAC)₃, Co(Bipy)₃ (ClO₄)₃ etc.,
- (iii) the complex may form an irreversible oxygen carrier in which R_{α} values will be temperature independent. eg K₃Co(CN)₆ etc.,

(5) Effect of other Ambients

(26)
Yasukawa observed that traces of ethylene diamine vapours promoted annealing in trisethylene diamine Co (III) nitrate and also that ammonia gas promoted annealing in Co (NH₃)₆³⁺. On the basis of the present model, these are to be expected since the reformation reactions involving ligand deficient species and ligand will be promoted if ligand is present to a larger extent. However when these ambients (NH₃ or ethylene diamine) are used for trisacetylacetonone Co (III), no effects should be expected and this indeed the case (27).

As far as the effect of other ambients like No, acetone etc., on annealing and exchange (29) the present data is limited to one or two complexes so that it is futile to give rational explanation. However it is felt that either these ambients would form adsorbed species

$[\text{Co}(\text{NH}_3)_5 \text{No}]_2$ for instance or compete with oxygen in the sequence of oxidation reactions.

(6) Water of Hydration Effect

The role of water of hydration in promoting annealing and exchange can also be understood in terms of oxygen carrier formation.

Erskine and Field ⁽²⁵⁾ have shown that traces of water oxidises the cobaltous carrier to cobaltic form ; they have given the example of Co (II) (dimethyl glyoxime)₂. Thus the observations of Ramshesh ⁽²⁶⁾ for the faster annealing and exchange in $\left[\text{Co} (\text{dimethyl glyoxime})_2 (\text{NH}_3)_2 \right] \text{Cl} \cdot 5\text{H}_2\text{O}$ as compared to that in the anhydrous complex can be easily explained. The case of trisdipyridyl complex will be explained a bit later.

(7) Effect of Radiation, influence of pre and post irradiation on annealing

All these sets of experiments in various permutations viz., preirradiation, thermal annealing + Radiation annealing + Thermal annealing etc., can also be explained on the basis of the present models

(8) The case of trisdipyridyl Co (III) complex

Among all the complexes investigated cobalt trisdipyridyl perchlorate is unique in as much as the rate of annealing and exchange is very fast even at room temperature. In fact Amar Nath's ⁽⁴⁾ model was based mainly on the peculiarities exhibited by this complex. According to the author the peculiarities exhibited by this complex is not a general trend and that a specific effect is at work in this complex. This view is also shared by Venkateswarlu ⁽²⁾.

Burstal and Nyholm ⁽³⁰⁾ have shown that in trisdipyridyl Co(III), Co (II) trisdipyridyl is always present as an impurity and this leads to a fast electron transfer reaction between these two species. It is possible that this Co (II) species could dissociate easily or alternately undergo exchange with ^{*}Co(II) rapidly.

In fact such racemisation is completely absent in trisdipyridyl complexes of neighbouring elements. Burstal and Nyholm state that in tris dipyridyl perchlorate Ni (II) no racemisation is observed. This complex should therefore show neither exchange or annealing on a fast scale. This has indeed been observed by Ramshesh⁽²¹⁾ who showed that the rate of annealing of ⁵⁸Co formed in the nickel complex by ⁵⁸Ni (n,p) ⁵⁸Co and the rate of exchange in ⁵⁷Co doped complex is very low. However, the author feels that Co (III) trisdipyridyl complex is still peculiar and attempts to fit its data into any model is not justified.

CONCLUSION

Thus it is felt that the above model can explain most observations. A word of caution is necessary. The artifacts involved in dissolution, separation etc., introduce an uncertainty as far as the identity of the original species is concerned. At one stage it was thought that non destructive techniques like Mossbauer spectroscopy do indicate the exact species formed; however, as pointed out earlier Eugene Le May et al's⁽¹¹⁾ work and also the latest⁽³⁰⁾ observation indicates that the species formed on the surface is not necessarily the same as the ones in the bulk.

What is also not clear is whether the same set of mechanistic observations can explain the behaviour of oxyanions also. Here again the closeness in annealing and exchange experiments suggest that the order models need not be invoked. In fact Collins et al⁽³¹⁾ have suggested that in transfer annealing of *Cr³⁺ doped K₂CrO₄ or thermal annealing in n⁻ irradiated K₂CrO₄ the primary step could be dissociation or

ionisation of the chromate followed by electron transfer reaction. However, the author would not like to venture into that area.

Acknowledgements

The author would like to thank Dr. K. Narayana Rao, Head, Chemistry Division for critically going through the manuscript and suggesting modifications. He is thankful to his colleagues Dr. K. S. Venkateswarlu, Dr. A.R. Gupta and Dr. N.S. Chandrasekharaiah for useful discussions.

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Table 1^{*}

Exchange and Annealing in some cobalt complexes.

	Treatment	Exchange	Annealing
Co (ACAC) ₃	Initial	0.1	4.8
	Heated	33.0	66.6
Cyanocobalamin	Initial	0.4	4.8
	Heated	0.7	4.8
Co (bimethylglyceramine) ₃	Initial	0.8	10.4
	NH ₃ Cl.5H ₂ O Heated	5.1	25.0

(All heated samples refer to identical heat treatment for exchange and annealing)

* Taken from Ref. 7, 18, 19.

Table 2^{*}

D_{N-O} values and Exchange in M(ACAC)₃ Complexes

	Mn (ACAC) ₃	Fe(ACAC) ₃	Co(ACAC) ₃	Cr(ACAC) ₃
D _{N - O} (Kcal/mole)	41 ± 1	45 ± 1	47 ± 1	52 ± 1
% Exchange with *Co ²⁺				
Initial	23.5	1.0	1.0	1.0
24 hr. at 393 K	75.0	25.0	10.5	5.5

* Taken from Ref (16), (20), (22)

In Mn (AC AC)₃ the data is somewhat complicated due to photo decomposition of the complex.

